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BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS ORSAY

1927

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ANNULÉ
BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS - ORSAY

CONTENTS OF VOLUME XXXI

1. JANUARY

E. A. Cooper and Edgar Sanders, — On the Relation of Phenol to Proteins and other Colloids, ... 1
H. H. Lowry and G. T. Kohman, — The Mechanism of the Absorption of Water by Rubber, ... 23
L. J. P. Keffler and F. C. Guthrie, — Investigation on the Heats of Combustion of Proposed Secondary Standard Substances and on Position and Optical Isomers, ... 58
Wilder D. Bancroft, — The Mass Unit of the Chemical Potential, ... 69
J. H. Coste, — On the Solubility of Pure and Atmospheric Nitrogen in Distilled and Sea Water, ... 81
L. H. Reyerson and L. E. Swearingen, — The Adsorption of Gases by Metallized Silica Gels, 88
J. N. Pearce and C. N. Ott, — A Study of the Mechanism of the Catalytic Decomposition of Esters by Nickel, ... 102
H. A. Taylor, — The Decay of Phosphorescence of Zinc Sulphide, ... 115
R. C. Cantelo, — The Methane Equilibrium. II, ... 124
J. W. McBain, H. S. Howes and Muriel Thorburn, — The Hydrogen Electrode in the Study of the Rate of Saponification of Oils and Fats by Aqueous Alkali, ... 131
New Books, ... 144

2. FEBRUARY

M. G. Mellon and F. D. Martin, — Solutions for Colorimetric Standards. I, ... 161
Milton Bergstein, — The Catalytic Minimum Point. II, ... 178
S. Ghosh and N. R. Dhar, — Studies in Adsorption. XVII, ... 187
O. K. Rice, — Dynamic Surface Tension and the Structure of Surfaces, ... 207
H. A. Taylor and W. A. Wesley, — The Gaseous Reaction between Hydrogen Sulphide and Sulphur Dioxide, ... 216
J. N. Pearce and R. D. Snow, — An Improved Dynamic Method for measuring Vapor Pressures, ... 231
R. C. Cantelo, — The Methane Equilibrium. II, ... 246
Enoch Swan and A. R. Urquhart, — Adsorption Equations, ... 251
W. A. Dew and H. S. Taylor, — Adsorption and Heat of Adsorption of Ammonia Gas on Metallic Catalysts, ... 277
L. E. Bowe, — The Neutral Salt Effect, ... 291
New Books, ... 303

3. MARCH

C. W. Mason, R. W. Harman, — Structural Colors in Insects. II, ... 321
H. A. Taylor and R. R. Denslow, — Aqueous Solutions of Sodium Silicates. V, ... 355
Emil Hatschek, — The Thermal Decomposition of Nitrosyl Chlorides, 374
V. K. LaMer and T. H. Gronwall, — The Apparent Viscosity of Colloidal Solutions, ... 383
P. B. Ganguly, — The Partial Molal Volumes of Water and Salt in Solutions of the Alkali Halides, ... 393
Diffusion of Aqueous Sodium Silicate Solutions across Semipermeable Membranes, ... 407

ANNULÉ

R. C. Cantelo,	The Methane Equilibrium. IV,	417
K. C. Sen,	Adsorption by Metallic Hydroxides. I,	419
Wilder D. Bancroft and Charles Gurchot,	Cell Mitosis,	430
G. S. Parks and Clare S. Chaffee,	Some Physical Chemical Properties of Mixtures of Acetone and Isopropyl Alcohol,	439
I. P. Baughman,	The Study of the Tannin-Gelatin Reaction,	448
A. F. Scott, and W. R. Frazier,	The Solubilities and Densities of Saturated Solutions of Sodium and Potassium Halides at 25°	459
R. A. Gortner and Walter F. Hoffman,	The Imbibition of Gelatin dried as a Gel and as a Sol,	464
New Books,		467

4. APRIL

P. B. Ganguly,	Studies in the Formation of Liesegang Rings,	481
R. E. Gibson,	The System Sodium Sulphate-Water,	496
R. W. Harman,	Aqueous Solutions of Sodium Silicates. VI,	511
J. W. Williams and T. A. Whitenack,	The Application of the Electron Tube to Potentiometric Titrations,	519
K. C. Sen,	Adsorption by Metallic Hydroxides. II,	525
P. G. Nutting,	The Adsorptive Force of Silica for Water,	531
D. H. Peacock,	The Velocity of Reaction and Energy of Activation of Halogen Compounds,	535
E. C. Gilbert,	The Effect of Higher Aliphatic Acids on the Surface Tension of a Heavy Hydrocarbon Oil,	543
J. R. Pound,	The Electrical Conductivities of Some Solutions in Aniline,	547
J. W. McBain and John Ferguson,	On the Nature of the Influence of Humidity Changes upon the Composition of Building Materials,	564
R. E. Burk,	A Gage for the Measurement of High Vacua,	591
Alan Leighton and O. E. Williams,	The Basic Viscosity of Ice-Cream Mixes,	596
H. M. Trimble,	The Coalescence of an Unfilterable Precipitate of Barium Sulphate,	601
W. C. Hansen, W. Dyckerhoff, F. W. Ashton and R. H. Bogue,	Studies on the System Lime-Alumina-Silica,	607
R. W. Harman,	Aqueous Solutions of Sodium Silicates. VII,	616
H. G. Halvorson and R. L. Starkey,	Studies on the Transformation of Iron in Nature. I,	626
New Books,		632

5. MAY

W. E. Garner, D. McKie and B. C. J. G. Knight,	The Area of the Internal Surface of Charcoal as Determined by the Adsorption of Normal Aliphatic Alcohols from Aqueous Solution,	641
S. Ghosh and N. R. Dhar,	Studies in Adsorption. XVIII,	649
B. Bruzs,	Corresponding States for the Entropy of Elements,	681
K. C. Sen,	Adsorption by Metallic Hydroxides. III,	686
C. R. Pitts,	The Ionization obtained by bubbling Air through Various Solutions,	693
S. B. Hendricks and R. W. G. Wyckoff,	The Positions of the K-Absorption Limits of Vanadium in Various of its Compounds,	703
E. R. Riegel and M. C. Reinhard,	The Zone Pattern formed by Silver Dichromate in Solid Gelatine Gel,	713
Sam Lenher and I. R. McHaffie,	The Free Energy Change in Adsorption at a Solid-Vapor Interface,	719

R. A. Morton and R. W. Riding,	The Refractivity of Carbon Monoxide,	723
E. B. Holland and G. M. Gilligan,	Solubility of Copper Sulphate, Malachite, and Burgundy Precipitate in Ammonium Hydroxide, Carbonate and Bicarbonate,	728
F. P. Worley and J. C. Andrews,	Mutarotation. I,	742
R. D. Kleeman,	The Absolute Zero of the Externally Controllable Entropy and Internal Energy of a Substance or Mixture,	747
J. B. Ferguson,	The System Water-Phenol,	757
E. O. Kraemer and S. T. Dexter,	The Light-Scattering Capacity (Tyndall Effect) and Colloidal Behavior of Gelatine Sols and Gels,	764
New Books,		783

6. JUNE

P. H. Fall,	Detergent Action of Soaps,	801
J. H. Wolfenden, W. Jackson and H. B. Hartley,	Heats of Ionization in Methyl Alcohol,	850
F. A. Madenwald, C. O. Henke and O. W. Brown,	Catalytic Activity of Lead,	862
F. F. Nord,	Influence of Heat and Hydrogen Ion Concentration on Biological Transportation Systems containing Sulphur,	867
T. S. Eckert and W. G. France,	The Effect of Gelatin upon the Size and Distribution of Macroscopic Crystals grown from Aqueous Solutions,	877
J. C. Andrews, and F. P. Worley,	Mutarotation. II,	882
R. H. Gerke and J. R. Geddes,	An Improved Hydrogen Electrode Vessel and the Electromotive Force of the Mercury, Mercurous Bromide, Bromide Ion Electrode,	886
A. N. C. Bennett,	Some Vapour Pressures and Activities of Aqueous Solutions of Sodium Silicates,	890
J. C. W. Frazer, W. A. Patrick and H. E. Smith,	The Thickness of Adsorbed Vapor Films,	897
B. H. Carroll and Donald Hubbard,	The Photographic Emulsion. I,	906
K. C. Sen,	Adsorption by Metallic Hydroxides. IV,	922
Florence Bush,	The Color of Silver Chromate,	931
Tutomu Maeda,	Some Remarks on the Colloidal Theory of Cements,	933
R. D. Kleeman,	Properties of Substances and Mixtures in the Condensed State at the Absolute Zero of Temperature,	937
New Books,		948

7. JULY

H. W. Walker,	Catalytic Reactions of Ethylene,	961
M. N. Chakravarti and N. R. Dhar,	Studies in Adsorption. XIX,	997
F. W. Laird,	Sedimentation of Colloidal Particles,	1034
E. C. Gilbert and B. E. Lauer,	A Study of the Ternary System: Methyl Benzoate, Methanol, and Water,	1050
H. D. Gibbs,	Phenol Tests. IV,	1053
R. M. Hann and G. L. Keenan,	The Optical Identification of the Naphthalene Sulphonic Acids by means of their Benzyl-Pseudo-Thiourea Salts,	1082
W. L. Chandler and E. J. Miller,	Colloidal Iodine,	1091

S. C. Collins,	A New Thermoregulator,	1097
W. S. Funnell, and G. I. Hoover,	An All-Glass Gas-Circulating Apparatus,	1099
F. M. Brewer, and L. M. Dennis,	Germanium. XIX,	1101
New Books,		1106
	8. AUGUST	
E. E. Reid,	Fifth Report of the Committee on Contact Catalysis,	1121
C. W. Sweitzer,	Light-Scattering of Aqueous Salt Solutions,	1150
F. G. Soper,	The Rate of Transformation of Acetylchloroaminobenzene into o- and p-Chloroanilides as a measure of the Catalytic Power of Hydrochloric Acid,	1192
E. J. Miller,	Adsorption from Solution by Ash-free Adsorbent Charcoal. III,	1197
H. A. Taylor and C. F. Pickett,	The Decomposition of Hydrogen Sulphide,	1212
V. N. Morris and L. H. Reyerson,	The Catalytic Activity of Metallized Silica Gels. I,	1220
H. A. Fells and J. B. Firth,	The Function of Water Present in Silicic Acid Gel,	1230
H. B. Weiser and A. D. Garrison,	The Rôle of Water in the Photochemical Decomposition of Zinc Sulphide,	1237
E. R. Washburn,	The Creeping of Solutions,	1246
R. H. Lambert and E. P. Wightman,	Thermodynamic Possibilities of the Silver Sulfide Bromine-Acceptor Hypothesis of Latent Image Formation,	1249
N. R. Dhar,	Relation between the Metabolism of Glucose and Fats in Diabetes,	1259
R. C. Smith and Miss I. C. Dow,	The Drop Number and Emulsifiability,	1263
W. M. Latimer,	The Electrode Potentials of Beryllium, Magnesium, Calcium, Strontium, and Barium from Thermal Data,	1267
New Books,		1270
	9. SEPTEMBER	
G. P. Vincent,	Detergent Action of Soaps. II,	1281
E. R. Jones,	Some Observations on the System Phenol-Water,	1316
George Glockler,	Ionization produced by Radon in Spherical Vessels,	1322
V. N. Morris and L. H. Ryerson,	The Catalytic Activity of Metallized Silica Gels. II,	1332
Dean Burk,	Photosynthesis with Ammonia,	1338
F. O. Rice and O. M. Reiff,	The Thermal Decomposition of Hydrogen Peroxide,	1352
C. W. Tucker,	A Study of Photovoltaic Cells,	1357
George Lynn,	A Convenient Form of Apparatus for the Determination of Melting Temperature,	1381
H. B. Weiser and E. E. Porter,	The Physical Chemistry of Color Lake Formation. I,	1383
H. M. Dawson,	The Signification of Isocatalytic Data and the So-called Protion Theory of Chemical Reactivity,	1400
E. D. Botts and F. C. Krauskopf,	Some Electrochemical Studies of Titanium,	1404
J. D. Stranathan and John Strong,	Viscosities, Electrical Conductivities, and Specific Volumes of Acetic Acid-Stannic Chloride Solutions,	1420

K. M. Tressler and L. M. Dennis,	Germanium. XX,	1429
L. J. Waldbauer and I. J. Patton,	On the Nature of Activated Molecules,	1433
New Books,		1435
	10. OCTOBER	
C. A. Amick,	The Copper Number for Glucose,	1441
P. B. Taylor,	Electromotive Force of the Cell with Transference and Theory of Interdiffusion of Electrolytes,	1478
Wilder D. Bancroft,	Gibbs on Adsorption,	
F. O. Rice and M. L. Kilpatrick,	The Photochemical Decomposition of Hydrogen Peroxide Solutions,	1501
W. A. Patrick, J. C. W. Frazer and R. I. Bush,	A Study of the Structural Changes in Amorphous Materials, Silica Gel	1511
S. Venkateswaran,	Compressibilities of Aqueous Solutions of Some Fatty Acids,	1521
F. M. Brewer and L. M. Dennis,	Germanium XXII,	1526
P. G. Colin and H. V. Tartar,	A Laboratory Study of Nitrogen Fixation by the High-Tension Arc,	1539
R. D. Kleeman,	Properties at the Absolute Zero of Temperature of the quantities associated with the Reversible Mixing of Substances,	1559
A. J. Scarlett, W. L. Morgan and J. H. Hildebrand,	Emulsification of Solid Powders,	1566
F. O. Rice and Dorothy M. Getz,	A Study of the Thermal Decomposition of Nitrogen Pentoxide,	1572
S. G. Mokrushin,	On the Contraction of Molecules in the Liquid State,	1581
New Books,		1584
	11. NOVEMBER	
H. H. Lowry and P. S. Olmstead	The Adsorption of Gases by Solids with special reference to the Adsorption of Carbon Dioxide by Charcoal,	1601
William Lerch and R. H. Bogue,	Studies on the Hydrolysis of Compounds which may occur in Portland Cement,	1627
W. F. K. Wynne-Jones,	The Correction of Conductivity Data for the Conductivity of the Solvent,	1647
Alan Leighton and O. E. Williams,	The Effect of Temperature on the Basic Viscosity of Ice-Cream Mixes,	1663
R. D. Kleeman,	The Internal Energy, Maximum Work, and Free Energy of the Elements,	1669
J. W. McBain and W. B. Lee,	Adhesives and Adhesion: Gums, Resins and Waxes between Polished Metal Surfaces,	1674
Wilder D. Bancroft and C. W. Tucker,	Gibbs on Emulsification,	1681
Lyman J. Wood,	A Study of Annealing Effects of Certain Copper-Nickel-Aluminum-Manganese Alloys,	1693
H. B. Weiser and E. E. Porter,	The Physical Chemistry of Color Lake Formation II,	1704
L. M. Dennis and S. M. Joseph,	Germanium. XXIII,	1716
Irving Langmuir and D. B. Langmuir,	The Effect of Monomolecular Films on the Evaporation of Ether Solutions,	1719
L. T. M. Gray,	Studies in the Experimental Technique of Photochemistry. IV,	1732
J. H. Perry,	The Vapor Pressures of Methylene Chloride,	1737

R. M. Woodman,	On the Causes of Solubility,	1742
Jacob Papish and F. E. Agel,	Composite Yellow,	1746
New Books,		1748

12. DECEMBER

L. E. Dodd,	A Method for comparing the Times of Mixing of Two Transparent Liquids in Different proportions, and Some Experimental Results, particularly with Gasoline and Carbon Bisulphide,	1761
F. G. Soper,	The Velocity of Interaction of Ions,	1790
S. L. Bigelow and H. M. Trimble,	The Relation of Vapor Pressure to Particle Size,	1798
F. M. Brewer,	Germanium. XXIV,	1817
H. B. Weiser and E. E. Porter,	The Physical Chemistry of Color Lake Formation. III,	1824
K. C. Sen,	Adsorption by Metallic Hydroxides. V,	1840
G. S. Parks and H. M. Huffman,	Studies on Glass. I,	1842
C. W. Mason,	Structural Colors in Insects. III,	1856
D. C. Carpenter,	The Influence of Salts on the Optical Rotation of Gelatin. I,	1873
J. C. Andrews and F. P. Worley,	Mutarotation. III,	1880
Thomas Bell and Robert Wright,	The Partial Vapor Pressures of Benzene-Toluene and Benzene-Ethylbenzene Mixtures,	1886
New Books,		1887
Name Index,		1893
Index to New Books,		1900
Subject Index,		1902



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ORSAY

ON THE RELATIONS OF PHENOL TO PROTEINS; AND OTHER COLLOIDS. A CONTRIBUTION TO OUR KNOWLEDGE OF DISINFECTANT ACTION

BY E. ASHLEY COOPER AND EDGAR SANDERS

Introduction

The action of most disinfectants can be explained on the basis of some interaction between the disinfecting agent and the protein constituents of the organism. Formaldehyde, mercury compounds, and the halogens, all combine chemically with the proteins. Other germicides, in particular the phenols, although they cause distinctive changes in many proteins, do not appear to enter into chemical combination with them. It has long been known that phenol, like the aliphatic alcohols, behaves as a protein precipitant and the destruction of bacteria by hot water was found by Chick[1] to run parallel to the heat coagulation of the proteins. Hence the existence of a connection between the precipitation of proteins by phenol and its lethal action on bacteria was naturally inferred.

Such knowledge of these disinfectants as we possess however, dates from 1909, when Reichel[2] showed that phenol was absorbed reversibly from aqueous solution by the heat coagula of serum and egg-white. Later, Cooper and Woodhouse[3] carried out a series of quantitative studies on the relations between proteins and phenols, of which the more general conclusions may be summarised as follows:—

1. The uptake of phenol from aqueous solution by proteins first follows the partition law until a phenol concentration, fairly definite for each protein, is reached. At higher concentrations an increased phenol absorption follows accompanied by precipitation of the protein.

Albumin and globulin precipitated by other means, such as the heat coagula, also exhibit the same high solvent power for phenol.

2. A relation exists between the bactericidal power of a phenol and the concentration of it necessary to precipitate a protein. Phenols of high bactericidal power precipitate proteins at low concentrations and vice versa, but their precipitating power is not determined by their solubility in proteins alone.

Such a correspondence has been shown to exist in the case of phenol, m-cresol, the nitrophenols, chlorophenols, and aliphatic alcohols.

The disinfectant action of phenol thus appears to be dependent on its de-emulsifying action on the bacterial proteins.

The present work was undertaken to gain further information as to the nature of the change induced in proteins by the action of phenols, and to extend our knowledge of the fundamental problem concerning the mechanism of disinfection.

[1] J. Hygiene, **10**, 237 (1926).
[2] Biochem. Z., **22**, 149 (1909).
[3] Cooper: Biochem. J. **6**, 362 (1912); Cooper and Woodhouse: **17**, 600 (1923).

I. THE PRECIPITATION OF THE PROTEINS OF SERUM BY PHENOL

The albumin, pseudo-globulin, and euglobulin were prepared from serum by the usual fractionation methods with salt-solutions. The aqueous solutions of albumin and pseudo-globulin were dialysed to free from salts before use. The euglobulin was dialysed against 0.9% sodium chloride, in order to free from as much salt as possible and yet retain the protein in colloidal solution.

Each protein solution was diluted to a concentration of 0.3%.

The precipitation experiments.

The experiments were carried out in test tubes, using 1 c.c. of protein solution and 4 c.c. of phenol solution throughout. The protein solutions were adjusted to the isoelectric point, and the state of the protein was observed for varying phenol concentrations. Two blank tubes were made up with water in place of phenol. One was used as a comparison tube in detecting any slight turbidity after the addition of phenol; the other was boiled to see that the protein was readily coagulable, a condition which only obtains near the iso-electric point.

TABLE I. Serum Albumin

	Phenol Concentration	State of Protein
1.	0.08%	In solution.
2.	0.8 %	"
3.	1.2 %	Slight turbidity.
4.	1.4 %	Precipitate on standing.
5.	1.6 %	" " "
6.	1.8 %	Immediate coagulation.
7.	2.0 %	" "

The results show that the precipitation of serum albumin by phenol begins when the phenol concentration reaches about 1%. The filtrates from 4 and 5 gave faint positive reactions for protein. In 6 and 7 however, the protein had been completely thrown out of solution. It is therefore about as sensitive to precipitation as egg-albumin which is completely coagulated by 1.45% phenol (l. c. 1923).

The filtrates from 10 and 11 showed very faint positive reactions for protein.

The effect of phenol on pseudo-globulin thus appears to start at the very lowest concentrations—as low as 1/1000—and to increase with rising phenol concentration, until at about 2% complete precipitation takes place.

It has been shown that phenol exerts a disinfectant action at very low concentrations. Thus Bacillus coli are killed by a concentration of 1/500, while a concentration of 1/900 proves fatal to Bacillus pyocyaneus. Hence in bacteria, there presumably exist proteins capable of coagulation at these concentrations. This theory therefore receives support from the above results with pseudo-globulin.

TABLE II. Pseudo-Globulin

	Phenol Concentration	State of Protein
1.	0.08%	Gradually increasing turbidity with slight precipitation on long standing.
2.	0.2	
3.	0.24	
4.	0.32	
5.	0.4	
6.	0.8	Turbidity with precipitate separating in 1–5 hours.
7.	1.2	
8.	1.4	
9.	1.6	
10.	1.8	Coagulation, precipitate separating at once.
11.	2.0	

TABLE III. Euglobulin. (dissolved in 0.9% sodium chloride solution)

	Phenol Concentration	State of Protein
1.	0.08%	In solution.
2.	0.32%	"
*3.	0.55%	Slight turbidity.
*4.	0.84%	Precipitation on long standing.
*5.	1.15%	
*6.	1.25%	Precipitation in an hour.

* (Owing to shortage of protein, phenol solution was added to previous tubes, giving the concentration shown in Col. 1.)

The filtrate from 6 gave only a faint reaction for protein. The coagulation of euglobulin by phenol therefore begins at a concentration of about 0.5% and it is completely thrown out of solution by about 1.5% of phenol. It is more sensitive to precipitation than serum albumin. On the other hand, the phenol concentrations necessary to produce *complete* separation of protein are not greatly different:—

Egg-albumin	1.5%	(Cooper and Woodhouse.)
Serum albumin	1.8%	
Pseudo-globulin	2.0%	
Euglobulin	1.5%	

Similar results were obtained by Tebb[1] in studying the action of alcohol upon the foregoing proteins.

II. THE DISTRIBUTION OF PHENOL BETWEEN WATER AND THE SERUM PROTEINS

Measurements of the partition of phenol between water and gelatin, egg-albumin, and casein, were carried out by E. A. C. in 1912, the investigations being later extended to the chlorphenols. (l. c. 1923.)

The relative solubilities of phenol in water and the serum proteins have now been investigated to ascertain whether any relation exists between the solubility of phenol in a protein and its precipitating action thereon.

[1] Halliburton: "Biochemistry of Muscle and Nerve," p. 24.

Details of the experiments.

The method employed was similar to that described in the earlier work. A measured volume of the protein solution is introduced into a dialyser which is immersed in a known volume of phenol solution contained in a stoppered bottle. The phenol solution is estimated by Lloyd's method[1] before and after distribution and hence the solubility ratios can be determined—i.e. the ratio of the weight of phenol in 1 grm. of protein to the weight of phenol in 1 c.c. of solution in the equilibrium condition.

Subsequent dilution of the outer solution enables the reverse process—the passage of phenol from protein to water—to be followed.

The phenol, in Lloyd's method, is brominated in acid solution to give tribromphenol. Hydrochloric acid is added to the phenol solution and an excess of standard sodium hypobromite solution run in from a burette. The excess of bromine is estimated, after the addition of potassium iodide, by titration with standard sodium thiosulphate solution.

The dialysers employed in a preliminary experiment were of parchment paper, but it was found that organic matter was extracted from the parchment, giving erroneous results in the estimation of the phenol solutions. *Viscose* thimbles were therefore finally employed, as they caused no interference with the phenol titrations, were freely permeable to phenol, and did not absorb phenol from aqueous solution.

TABLE IV. Serum Albumin

Inside dialysers: 20 c.c. 4.09% albumin solution.

Outside dialysers: 30 c.c. phenol solution.

	Phenol Concentration Initial %	Final %	Phenol in 1 gm. protein	State of protein	Distribution ratio
1R.	0.149%	0.166	0.019	Dispersed	11.5
1.	0.296	0.248 (.248)	0.029	"	11.8
2R.	0.362	0.415	0.049	"	11.8
2.	0.749	0.637 (.637)	0.068	"	10.7
3R.	1.49	1.66	0.199	Heavy ppt.	11.9
4R.	2.07	2.32	0.28	" "	12.1
3.	2.99	2.49 (2.54)	0.306	" "	12.3
4.	4.16	3.45 (3.45)	0.434	" "	12.6

The lower phenol concentrations were analysed after seven days. With the higher concentrations, where a heavy protein clot was formed, fourteen days were allowed for equilibrium to become established. The analyses were repeated after a further twelve days, the results of the second analysis being shown in brackets in column 2. The very good agreement between the two sets of figures shows that true equilibrium had been reached.

The results marked "R" in the table were obtained by diluting the outer solution in each bottle, 20 c.c. of phenol solution being replaced by 20 c.c. of water. Two sets of equilibria were thus determined, one set while the phenol concentrations were successively raised, the other by the reverse

[1] J. Am. Chem. Soc., 27, 23 (1905).

process. The coincidence of the two sets of readings indicates that the absorption of phenol by serum albumin is a reversible process.

The high distribution ratios obtained are characteristic of a precipitated protein, similar figures having been previously found for egg-albumin after precipitation had taken place. No low distribution ratios (about 3 for egg-albumin) such as appear to characterise the emulsoid condition, have been obtained.

The constancy (within experimental error) of the distribution ratio is well marked, showing that the partition law strictly held. Phenol may thus be considered to form a true solution in the protein phase. It is remarkable that, whilst the partition-coefficient for dispersed egg-albumin is 3, in the case of dispersed serum-albumin it averages 11, although the two proteins are precipitated by phenol at about the same concentration. Evidently the precipitating action of phenol is not primarily determined by the absolute amount dissolved within the protein phase.

TABLE V. Pseudo-Globulin

Inside dialysers: 20 c.c. 2.61% globulin solution.
Outside " 30 c.c. phenol solution.

	Phenol Concentration Initial %	Final %		Phenol in 1 gm. protein	State of protein	Distribution ratio
1R.	0.166	0.173		0.0115	Turbidity.	6.6
1.	0.296	0.277	(.277)	0.0182	"	6.6
2R.	0.414	0.426		0.045	"	10.6
2.	0.749	0.690	(.690)	0.0565	"	8.2
3R.	1.608	1.706		0.203	Ppt.	11.9
4R.	2.21	2.39		0.284	"	11.9
3.	2.99	2.68	(2.68)	0.297	"	11.1
4.	4.16	3.69	(3.69)	0.450	"	12.2

The lower phenol concentrations were analysed after seven days, the higher ones after fourteen days. The analyses were repeated after a further twelve days. The two sets of analyses, shown side by side in column 2, are identical in each case. True equilibrium had therefore been reached.

Equilibria marked "R" were obtained, as described under serum albumin, while the phenol concentrations were successively diminished. The results show that the absorption of phenol by pseudo-globulin is not a strictly reversible process. The protein, after precipitation by phenol, retained its high solvent power for that substance. More phenol was held by the globulin during descending than during ascending phenol concentrations. In this respect it resembles egg-albumin.

Even at the lowest phenol concentration employed, the protein showed signs of precipitation. Hence no distribution ratios have been outlined for the protein in the emulsoid state. The ratios of 6.6 however, probably represent the transition period where the condition of the protein is beginning to change, the ratios then rising sharply to about 12, a partition coefficient of the same value as that obtained with coagulated serum-albumin. The solubility of phenol in widely different proteins is thus of much the same order.

III. THE PRECIPITATIONS OF MUSCLE PROTEINS BY PHENOL

Of the two proteins present in meat, paramyosinogen and myosinogen, the former is characterised by the low heat coagulation temperature of 47°C. Precipitation experiments were carried out with these proteins to ascertain if any quantitative relation held between the temperature of coagulation by heat and the concentration of phenol necessary to cause complete prectipitation.

Exactly the same procedure was adopted throughout as with the serum proteins.

TABLE VI. Myosinogen

	Phenol Concentration	State of Protein
1.	0.4%	In solution.
2.	0.8%	Turbidity.
3.	1.2%	Ppt. on standing.
4.	1.6%	" " "
5.	2.0%	Immediate ppt.

Qualitative tests made on the filtrates showed that precipitation was complete at a final concentration of 1.2% of phenol.

TABLE VII. Paramyosinogen

	Phenol Concentration	State of Protein
1.	0.2%	Slight opalescence.
2.	0.4%	Ppt. on standing.
3.	0.8%	Ppt.
4.	1.2%	"
5.	1.6%	"

Precipitation was complete at a final phenol concentration of 0.8%.

Paramyosinogen, which is coagulated at the lower temperature, is thus seen to be precipitated by phenol at lower concentrations than myosinogen. This relationship suggests an underlying similarity in the mechanism of the action of heat and phenol on proteins. Comparable results were obtained by Tebb (l. c.) in the case of alcohol.

IV. THE DISTRIBUTION OF PHENOL BETWEEN WATER AND EDESTIN

An examination of the behaviour of phenol with edestin was of interest, as no work had been previously carried out with a vegetable globulin. Cooper and Woodhouse (l. c.) however, had previously shown that it was precipitated from saline solution by phenol and the chlor-phenols.

Puré edestin was employed, and as the protein is quite insoluble in water, no dialysers were necessary. The equilibrium mixture was filtered from protein and the phenol estimated in a known volume of the clear filtrate.

To ensure that no protein passed the filter, a blank was employed—using ½ gm. edestin and 30 c.c. water.

10 c.c. hypobromite soln.	= 32.80 c.c. N/20 *thio.*
With 10 c.c. filtered	= 32.65 c.c. " "
extract	0.15 c.c.

The analyses were carried out after 3 days.

TABLE VIII

	Phenol concentration Initial %	Final %	Phenol absorbed by 1 gm. edestin	Distribution ratio
1.	0.200	0.183	0.010	5.6
2.	0.500	0.453	0.028	6.3
3.	1.00	0.889	0.066	7.4
4.	2.50	2.09	0.246	11.8

0.5 gm. edestin: 30 c.c. phenol solution.

Edestin thus appears to behave in a manner analogous to casein (E.A. C. l. c.), the distribution-ratio increasing with rising concentration.

This increase in distribution-ratio is not apparent in the case of the coagulated albumins and globulins, but was previously found to occur only with casein. The results may mean that the phenol molecules undergo actual *association* in edestin and casein, as is known to occur in benzene.

V. THE SOLUBILITY OF PHENOL IN GLIADIN

The class of proteins known as the prolamines or gliadins show a marked contrast in their solubility to all other proteins whether of animal or vegetable origin. Wheat gliadin, for example, dissolves in dilute alcohol of about 70% strength while it is quite insoluble in both water or absolute alcohol. It therefore seemed likely that gliadin might exhibit points of special interest in its behaviour with phenol.

A series of experiments were carried out with gliadin and phenol in different solvents:—

1. Water: protein insoluble.
2. 70% alcohol: protein soluble.
3. *Absolute alcohol: protein insoluble.*

It was hoped that a comparison of the solubilities of the protein for phenol in the three cases might throw some light on the change in the condition of proteins brought about by phenol precipitation.

The Distribution of Phenol between Gliadin and Water

Experiment A.

As the protein appeared to be quite insoluble in water, dialysers were dispensed with and the filtered solutions were analysed as described in the experiments with edestin. A blank experiment was performed using water in place of phenol solution. The analyses were carried out after four days.

TABLE IX

0.5 gm. gliadin : 30 c.c. phenol solution.

Blank. 10 c.c. hypobromite alone = 32.10 c.c. N/20 thiosulphate.
With 10 c.c. extract = 29.80 c.c. " "

2.30 c.c.

	Phenol concentration Initial %	Final %	Phenol absorbed by 1 gm. gliadin	Distribution ratio
1R.	0.189	0.212	0.023	11.0
1.	0.441	0.379	0.037	9.9
2R.	1.027	1.217	0.161	13.2
2.	2.51	2.05	0.275	13.4
3R.	1.98	2.35	0.341	14.5
3.	4.90	3.96	0.566	14.3

The blank experiment shows that a small quantity of protein was passing the filter. To allow for this 2.3 c.c. were added to the volumes of thiosulphate solution required in the subsequent estimations.

The equilibria marked "R" were obtained by diminishing the phenol concentrations, 15 c.c. of phenol solution being replaced by 15 c.c. of water. The coincidence of the two sets of results indicates that the distribution of phenol between gliadin and water is of a reversible nature.

The distribution ratios show the high solvent power of gliadin for phenol which is of the same order as that of other precipitated proteins. The tendency for the ratio to increase with ascending phenol concentration is suggestive of molecular association, as seemed to take place in casein and edestin.

The Distribution of Phenol between Gliadin and Water, Dilute Alcohol, and Absolute Alcohol

Three sets of equilibria were determined.

1. Phenol between gliadin and water, in which the protein is insoluble.
2. Between gliadin and 70% alcohol, in which the protein is soluble.
3. Between gliadin and absolute alcohol, which has no solvent action on the protein.

In the second of the three cases, dialysers had to be employed, as the protein was in solution. In order to obtain a strict comparison, dialysers were also employed in the other two cases. The distribution experiment with phenol between gliadin and water was therefore repeated using a viscose dialyser.

Gliadin and Water

Experiment B—with viscose dialyser.

The analyses were carried out after five days.

The results were obtained by successively diluting the outer solution in 1, i.e. all the equilibria were determined with the same portion of protein and the same dialyser.

The results are substantially the same as those obtained in Experiment A.

TABLE X

Inside dialyser : 0.5 gm. gliadin : 20 c.c. water.
Outside " 30 c.c. phenol solution.

	Phenol concentration Initial gm./100 cc.	Final gm./100 cc.	Phenol absorbed by 1 gm. gliadin gm.	Distribution ratio
I.	4.13	3.65	0.474	13.0
IR.	2.74	2.90	0.348	12.0
IRR.	2.17	2.28	0.265	11.6
IRRR.	1.707	1.801	0.190	10.5

Gliadin and Dilute Alcohol

Experiment A—with viscose dialyser.

It was found that phenol dissolved in dilute alcohol diffused only slowly through viscose and hence the distribution of phenol between gliadin and dilute alcohol was, under these conditions, likely to take many weeks to reach equilibrium.

Experiment B—with parchment dialysers.

It seemed probable that organic matter present in parchment paper would be insoluble in alcohol, thus making it practicable to use parchment dialysers in place of viscose. Both the dialysers and the alcohol were examined as possible sources of error.

10 c.c. hypobromite solution alone	= 34.2	c.c. N/20	thiosulphate.
With 10 c.c. of absolute alcohol	= 33.75	c.c. "	"
Br used up by alcohol	= 0.45	c.c. "	"
10 c.c. hypobromite solution alone	= 34.20	c.c. "	"
With 10 c.c. parchment extract in 70% alcohol	= 33.30	c.c. "	"
	0.90	c.c.	

The bromine used up by the alcohol and the parchment impurities together, is therefore equivalent to 0.9 c.c. of sodium thiosulphate solution. This control was neglected in the analyses, as the phenol solutions were diluted ten times before estimation.

The analyses were made after six days and again after a further four days.

TABLE XII

Inside dialyser, 0.5 gm. gliadin : 25 c.c. 70% alcohol.
Outside " 25 c.c. 6.97% phenol in 70% alcohol.

Time allowed	Initial conc. outside dialyser	Final conc. outside dialyser	Conc. for complete diffusion
	gm./100 cc	gm./100 cc	gm./100 cc
6 days.	6.97	3.61	3.49
10 days.	6.97	3.63	3.49

The phenol solutions thus diffused readily through parchment dialysers, the diffusion being complete in six days. No phenol however was taken up by gliadin from dilute alcohol solution.

Gliadin and Absolute Alcohol

Phenol dissolved in absolute alcohol diffused with extreme slowness through viscose. Hence parchment dialysers were used in these experiments.

The parchment was examined to see if soluble matter were extracted by absolute alcohol.

10 c.c. hypobromite alone	= 34.2 c.c.	N/20 thiosulphate.
With 10 c.c. alcoholic extract	= 33.5 c.c.	" "
	0.7 c.c.	" "

As the phenol solutions were diluted ten times before analysis, this blank of 0.7 c.c. was neglected.

The analyses were carried out after six days and again after a further four days.

TABLE XIII

Inside dialyser, 0.5 gm. gliadin : 25 c.c. absolute alcohol.
Outside " 25 c.c. 6.99% phenol in absolute alcohol.

Time allowed	Initial conc. outside dialyser	Final conc. outside dialyser	Conc. for complete diffusion
	gm./100 cc	gm./100 cc	gm./100 cc
6 days	6.99	3.50	3.50
10 days	6.99	3.52	3.50

Hence as in the case of dilute alcohol, no phenol is taken up by the protein. The explanation is apparently that already put forward by E. A. C. (l. c.)—the high solvent power of alcohol for phenol as compared with that of the protein. The fact that viscose is permeable to aqueous, but not to alcoholic phenol solutions points furthermore to association or to complex formation in the continuous phase.

VI. THE NATURE OF THE CHANGE PRODUCED BY PHENOL IN PROTEINS

Out knowledge of the precipitating action of phenol on proteins indicates a very close relationship between the protein—precipitating action of phenol and its lethal action on bacteria. The death of the organism appears to be due to the de-emulsification of the contained protein. The greatest interest therefore centers on this change in the state of the protein which is so intimately connected with the life process of the organism.

One of us (E. A. C.) showed that a protein coagulated either by heat or phenol, exhibited the same high solvent power for phenol, an observation which pointed to an analogy between the action of phenol and the action of

heat. Pauli[1], Lepeschkin[2] and others have shown that analogies exist between coagulation by alcohol, phenol, and hot water. Moreover, in a recent paper, Cooper and Forstner[3] have shown that those bacteria which are most susceptible to disinfection by alcohol and phenol are also most susceptible to the action of hot water.

It is known that heat coagulation occurs in two stages, first a denaturation, followed by agglutination. Thus a protein solution may be heated to 100°C. without coagulation taking place provided the solution is not at the iso-electric point. The protein undergoes denaturation in the process. Subsequent adjustment to the iso-electric point causes precipitation even though the solution be cold. Cooper and Woodhouse[4] showed that in a precisely similar manner, protein solutions may be treated with phenol without coagulation occurring. Adjustment in reaction however, even if the phenol be first removed by dialysis causes separation of a precipitate. This observation was originally made with egg-albumin, and the present authors have now confirmed the results with purified, crystalline serum-albumin.

It is apparently the second of these stages—agglutination—which is associated with increased solvent power of the protein for phenol, the denaturation which precedes coagulation having no effect on the distribution ratios (l. c. 1923). The increase in the uptake of phenol only appeared when the protein separated out as a precipitate. Moreover, salt solutions alone—inducing a partial dehydration of the protein—did not greatly increase the distribution ratio, but subsequent movement to the iso-electric point, however, caused a sudden rise in the ratios from 7.2 to 19.8. The authors therefore concluded that the increased partition-coefficient was associated with the separation of the protein in particulate form due to the electrical adjustment of the colloidal solution.

Considered from a general point of view, the precipitation of proteins by phenol may be due to chemical action, to causes purely physical in character or to both of these, one probably consequent on the other.

If the action be chemical in nature, replacement or substitution in the amino or carboxyl groups of the protein should have a profound influence on the phenol distribution. If the action be a physical one, due to the colloidal properties of protein solutions, other colloidal solutions should exhibit analogous behaviour with phenol.

Attempts have been made to test both these hypotheses experimentally.

A. The Distribution of Phenol between Water and Gelatin Derivatives

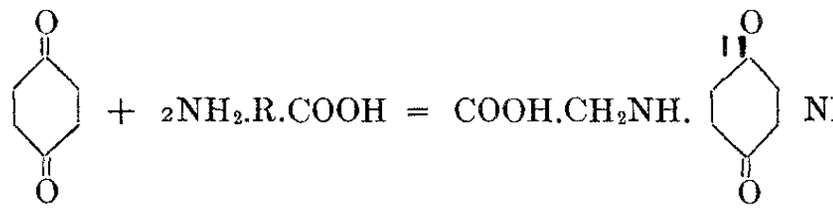
To test the first hypothesis, a number of gelatin derivatives were prepared, all of them by attacking the amino groups of the protein.

1. Formalised gelatin in which the hydrogen of some of the amino groups is replaced by the methylene radicle.

[1] Kolloid-Z., **5**, 164 (1909).
[2] Kolloid-Z., **32**, 42 (1923).
[3] Biochem. J., **18**, 141 (1924).
[4] Biochem. J., **17**, 600 (1923).

$$NH_2.CH_2.COOH + H.CHO = CH_2{:}N.CH_2.COOH + H_2O.$$

2. Quinone gelatin. The action of benzoquinone on proteins probably takes place thus:—



3. Brominated gelatin.

4. Desamino gelatin. In this case some of the amino groups are actually removed and replaced by hydroxyl; in the course of the complex action of nitrous acid on protein.

The experiment with gelatin itself was repeated for comparison with the results obtained with the derivatives.

Water and Gelatin

The gelatin was washed for two days in running tap-water, followed by several changes of distilled water. Water-soluble impurities were thus removed. After air-drying, the sheets were cut into narrow strips and dried in the steam oven.

The gelatin being quite insoluble in cold water, no dialysers were necessary, the phenol solutions being removed and analysed without filtration.

A control experiment was performed, using water in place of phenol solution to ensure that no protein material passed into solution.

TABLE XIV

2 gm. gelatin : 60 c.c. phenol solution.

Blank 10 c.c. hypobromite alone = 31.30 c.c. N/20 thiosulphate.

With 10 c.c. gelatin extract = 31.30 c.c. " "

0.00 c.c. " "

	Phenol concentration Initial	Final	Phenol absorbed by 1 gm. gelatin	State of protein	Distrib. ratio
	gm./100 cc	gm./100 cc	gm.		
1.	0.222	0.207	0.0045	unprecipitated	2.2
2.	0.500	0.468	0.0096	"	2.1
3.	1.000	0.931	0.0207	"	2.2
4.	2.500	2.31	0.056	"	2.4
5.	4.95	3.49	0.436	precipitated	12.5

The control experiment shows that no interfering material was extracted from the gelatin.

The results are in good agreement with the original figures obtained in a similar manner by E. A. C.

Water and Formalised Gelatin

10 gm. of the washed gelatin were treated with 600 c.c. of 40% formaldehyde for three days. The product was washed in successive changes of distilled water, until no more formalin could be detected in the washings, and was then dried at 100°C. The material was quite insoluble in water even on boiling.

A control experiment was performed substituting water for the phenol solution in order to detect any errors due either to soluble protein material or traces of formaldehyde.

The analyses were made after two days and in two cases again after a further four days, the result for the two analyses being shown side by side in column 2.

TABLE XV

2 gm. formalised gelatin : 60 c.c. phenol solution.
Blank 10 c.c. hypobromite alone = 30.80 c.c. N/20 thiosulphate.
With 10 c.c. extract = 30.80 c.c. " "
0.00 c.c. " "

	Phenol concentration Initial gm./100 cc	Final gm./100 cc	Phenol absorbed by 1 gm. formalised gelatin gm.	Distribution ratio
1.	0.222	0.200	.0066	3.3
2.	0.533	0.488 (.488)	.0135	2.8
3R.	0.447	0.500	.0155	3.1
3.	1.000	0.895	.0315	3.5
4R.	1.069	1.195	.071	5.8
4.	2.500	2.140 (2.12)	.109	5.1
5.	4.95	3.59	.405	11.3

The agreement between the analyses made after two days and after six days, shows that equilibrium had been reached in forty-eight hours.

The equilibria marked "R" were obtained by dilution of the phenol solutions. Their coincidence with the results obtained while the strength of the phenol solutions was being successively raised, indicates the reversible nature of the distribution.

The values for the distribution ratios are not very different from those obtained with gelatin itself. The low partition coefficient of 2 in the case of gelatin is exchanged for one of 4 (average) with the methylene derivative, which also exhibits the sudden rise in solvent power for phenol at higher phenol concentrations. No visible change however in the bulk of the protein accompanied this increase in solvent-power. Two strips only were precipitated as white sticky masses in exactly the same way as happens with gelatin. Notwithstanding, the distribution ratio, (11.3), is nearly as high as with gelatin (12.5) where all the protein is precipitated. Hence it appears that the change in the protein derivative which is responsible for the increased uptake of phenol need not necessarily manifest itself in a visible precipitation. With proteins themselves increased phenol absorption has always been accompanied by precipitation.

Water and Quinone-Gelatin

About 10 gm. of washed gelatin were treated for four days with a 1% solution of benzoquinone in water, washed thoroughly and dried at 90°C.

The product, resembling gelatin but deep ruby-red in colour, was completely insoluble in boiling water.

A blank experiment was carried out, replacing phenol solution by water, so that allowance might be made for any errors due to extraction of soluble matter from the protein derivative.

The phenol solutions were analysed after three days and again in two cases, at the end of a further four days, the results for the second analysis being shown bracketed in column 2.

TABLE XVI

1 gm. quinone-gelatin : 30 c.c. phenol solution.
Blank 10 c.c. hypobromite alone = 32.20 c.c. N/20 thiosulphate.
With 10 c.c. extract = 31.60 c.c. " "

0.60 c.c. " "

	Phenol concentration		Phenol absorbed by 1 gm. Quinone-gelatin	Distribution ratio
	Initial	Final		
	gm./100 cc	gm./100 cc	gm.	
1R.	0.129	0.134	.0072	5.4
1.	0.222	0.193	.0087	4.5
2.	0.443	0.393 (.389)	.015	3.8
3R.	0.591	0.621	.025	4.0
3.	1.000	0.886	.034	3.9
5RRR.	1.53	1.82	.067	3.7
4.	2.50	2.12 (2.13)	.116	5.5
5RR.	1.87	2.29	.156	6.8
5R.	2.29	2.80	.283	10.1
5.	4.88	3.43	.436	12.7

The control experiment shows that a small quantity of soluble matter was extracted from the gelatin derivative. To correct the error thus introduced, 0.6 c.c. was added to the volumes of thiosulphate solution required in the subsequent phenol titrations .

The agreement between the analyses made after three and after seven days shows that no further absorption of phenol had taken place. The distribution had reached equilibrium in three days.

The absorption was completely reversible, the equilibria obtained during descending phenol concentrations (marked "R") coinciding with those obtained during ascending concentrations of phenol. In fact, with the same portion of protein derivative a ratio of 12.7 was successively reduced to 10.1, 6.8 and 3.7 by diluting the phenol solution three times.

As with formalised gelatin, the partition coefficients for low phenol concentrations are greater than with gelatin. The coefficient of 2 in the case of gelatin became 4 with formalised gelatin and is raised to 4.5 (mean) with the quinone derivative.

The quinone-gelatin, although it showed no visible change throughout, yet exhibits the usual sharp rise in solvent power for phenol at higher concentrations. Hence the action of quinone or formaldehyde on gelatin, although it masks any visible precipitation due to the subsequent phenol action, does not prevent the change which is responsible for increased phenol up-take.

Water and Brominated Gelatin

10 gm. of the washed gelatin were treated for four days with saturated bromine water at room temperature. The product was washed in successive changes of distilled water, until no bromine could be detected in the washings. After air-drying the brominated gelatin was placed in the vacuum desiccator for two days.

The material was insoluble in hot water, but it gradually dissolved on prolonged boiling.

The analyses were carried out after two days and repeated in one case after a further four days.

The usual blank experiment was made with water in place of phenol solution.

TABLE XVII

1 gm. brominated gelatin : 30 c.c. phenol solution.
Blank 10 c.c. hypobromite alone = 32.10 c.c. N/20 thiosulphate.
With 10 c.c. extract = 31.10 c.c. " "

1.00 c.c. " "

	Phenol concentration		Phenol in 1 gm.	State of	Distribution
	Initial	Final	Br. gelatin	protein	ratio
	gm./100 cc	gm./100 cc	gm.		
1.	0.221	0.196	0.0069	unppt.	3.5
2.	0.441	0.405	0.0108	"	2.7
3R.	0.607	0.634	0.0201	"	3.2
3.	1.005	0.911	0.0282	"	3.1
4R.	1.45	1.63	0.049	"	2.9
4.	2.51	2.18	0.101	ppt.	4.6
5R.	2.29	2.80	0.287	"	10.3
5.	4.90	3.43	0.441	"	12.9
6.	6.86	4.47	0.717	"	16.0

The partition coefficients for low phenol concentrations are again higher than with gelatin itself, but slightly lower than those obtained with the formalin derivative.

Water and Desamino Gelatin

The production of the desamino derivative by the action of nitrous acid on gelatin was complicated by the fact that gelatin is soluble in acids. For the purposes of the distribution experiment, it was essential to use the derivative in a form similar to that of gelatin itself, in order that the results should be strictly comparable. In the final method used acetic acid and a slight excess of sodium nitrite were employed. After careful washing, the product was dried first in the air, then in the steam oven for ten hours. Any nitrogen gas still retained within the gelatin was then driven off. The dry product was yellow, but uniform in appearance.

Analyses of the phenol solutions were made after four and after eight days and the usual blank experiment was carried out.

TABLE XVIII

1 gm. desamino gelatin : 30 c.c. water.

Blank 10 c.c. hypobromite alone = 30.7 c.c. N/20 thiosulphate.
With 10 c.c. extract = 30.4 c.c. " "
0.3 c.c. " "

	Phenol concentration		Phenol in 1 gm. desaminogel.	State of protein	Distribution ratio
	Initial	Final			
	gm./100 cc	gm./100 cc	gm.		
1R.	0.304	0.316	0.0066	unppt.	2.1
1.	0.490	0.456	0.0102	"	2.2
2.	0.984	0.909	0.0225	"	2.5
3R.	1.42	1.60	0.044	"	2.7
3.	2.46	2.14	0.097	ppt.	4.5
4.	4.90	3.37	0.458	"	13.6
5R.	2.89	3.60	0.552	"	15.4
5.	6.88	4.33	0.765	"	17.7

In this case the low partition coefficients of 2, characteristic of gelatin itself, have been obtained. It is noteworthy that this is the only derivative in which the molecular weight of the gelatin has not been raised, the amino group being replaced by hydroxyl. The quinone derivative, in which the largest addition was made to the gelatin molecule, showed the largest increase in the partition coefficients for low phenol concentrations.

The results as a whole are of interest, inasmuch as they show that the substitution of the methylene group, the quinone nucleus, and bromine into the amino-groups of gelatin increases the solubility of phenol in the protein, yet treatment with nitrous acid has no effect on the partition coefficient.

B. The Behaviour of Phenol with other Colloids

(1) Suspensoid Colloids.

Phenol and ferric hydroxide sol.

A solution of "dialysed iron" was used and experiments were carried out in both the sol condition and with the coagulum produced by a trace of salt.

The results showed that the colloid did not absorb phenol.

Phenol and silver sol.

A concentrated silver sol was prepared by Carey Lea's method.

Table XIX

Inside dialyser, 10 c.c. silver sol.
Outside " 30 c.c. phenol solution.

	State of Colloid	Phenol concentration Initial	Phenol concentration Final	Phenol in approx. 1 gm. Ag	Approx. distrib. ratio
		gm./100 cc	gm./100 cc	gm.	
1.	Sol.	0.278	0.282	0.004	—
2.	"	3.72	3.67	0.04	1.1
3.	"	5.20	5.15	0.04	0.8
4.	Ppt.	3.72	3.75	——	—
5.	"	5.20	5.19	——	—

The fact that the quantity of phenol taken by the silver is identical in 2 and 3 suggests chemical action, for it is independent of the phenol concentration.

It appears from the figures for the precipitated sols that any phenol taken up in the sol condition is liberated when the sol is precipitated, the phenol concentrations returning to their original values. Thus:—

	2	3
Initial conc.	3.72%	5.20%
With Ag sol	3.67%	5.15%
With pptd. sol	3.75%	5.19%

The results with both iron and silver sols indicate that little, if any, phenol is absorbed by suspensoid colloids from aqueous solution.

(2) Emulsoid Colloids.

As the proteins themselves belong to the class of emulsoid colloids, it appeared probable that an investigation of the behaviour of other members of that group with phenol might be of value. For this purpose silicic acid and soaps appeared particularly well suited; for, while they closely resemble proteins from the colloid stand-point, chemically they are very different. A similar behaviour exhibited between phenol and silicic acid or soap as between phenol and protein would therefore very strongly suggest a physical interpretation of the foregoing observations.

Water and silicic acid.

Experiments showed that silicic acid did not absorb phenol from aqueous solution.

Water and sodium stearate.

As sodium stearate is practically insoluble in cold water, dialysers were not at first used, the solutions being merely filtered before analysis. With rising phenol concentration however, the soap gradually dissolved, and on acidification in the course of the phenol analyses a precipitate of fatty acid appeared and this underwent bromination, causing serious errors in the analyses. Viscose dialysers were therefore subsequently employed.

The analyses were made after five days and repeated in two cases after a further fourteen days. A blank experiment was carried out.

TABLE XX

Inside dialyser, 1 gm. sodium stearate : 10 cc. water.
Outside dialyser, 40 c.c. phenol solution.
Blank 10 c.c. hypobromite alone = 27.3 c.c. N/20 thiosulphate.
With 10 c.c. soap extract = 27.5 c.c. " "

0.2 c.c. " "

	Phenol concentration Initial	Final	Phenol in 1 gm. soap	Distribution ratio
	gm./100 cc	gm./100 cc	gm.	
1R.	0.176	0.183		
1.	0.297	0.294 (.296)	0.0015	0.5
2R.	0.416	0.423	0.0063	1.5
*2.	0.652	0.624	0.0084	1.3
3R.	0.972	1.064	0.0351	3.3
*3.	1.67	1.46	0.0627	4.3
4R.	1.64	1.98	0.144	7.2
*4.	3.28	2.46	0.246	10.0
5R.	2.62	3.25	0.275	8.5
5.	5.54	4.36 (4.36)	0.59	13.5

* (20 c.c. phenol solution outside dialyser.)

The soap dissolved gradually in the phenol solutions as the concentration of the latter rose. The solution outside the dialysers however were in every case free from soap, as judged by the absence of precipitate on acidifying. With the higher phenol concentrations a considerable quantity of water passed into the dialysers from outside.

The equilibria marked "R" were obtained during falling phenol concentrations, 10 c.c. of phenol solution being replaced by 10 c.c. of water. The results indicate that the absorption was reversible to some extent, but the figures are not uniform. The distribution ratios are of the same order as those obtained with gelatin, but whereas with gelatin increased phenol uptake was accompanied by precipitation of the protein, with sodium stearate it is associated with the passage of the soap into solution. In each case however the concentration of phenol in the water-phase is directly proportional

to the *square root* of the concentration in the colloid phase, giving then a constant partition-coefficient of about 2. This relationship also holds with the gelatin derivatives, (Tables XVI, XVII, XVIII), and may be associated with the gradual change in the condition of the colloid.

That the soap actually dissolved progressively with rising partition-coefficient is shown in the following experiments carried out in test tubes with 0.5 gm. sodium stearate, 5 c.c. water and 10 c.c. phenol solution. After standing some weeks the solutions were filtered and acidified, the presence of soap in solution being indicated by a precipitate of fatty acid.

Concentration of phenol solution added	Final phenol conc.	Behaviour of filtered solution with acid
%	%	
0.5	0.33	Trace of ppt.
1.0	0.67	" " "
1.5	1.00	Slight ppt.
2.0	1.33	" "
2.5	1.67	Ppt.
3.3	3.33	Heavy ppt.

Although the results are the converse of those obtained in the case of proteins, yet they have an interesting bearing on the interpretation of the relations of phenols to proteins. In the case of both soaps and proteins a change in the physical condition of the colloid can induce significant alterations in their solvent power for phenol, although the two classes of colloids are of quite different chemical nature. The results show the importance of fully considering physical factors in seeking an explanation of the phenomena described in the foregoing pages.

The investigations have shown that phenol and cresol are distributed between water and proteins in the emulsoid state according to the partition law, the partition-coefficient being in general 2-3 times as soluble in the proteins as in the water. At a certain phenol concentration the protein is precipitated, and this change in state is accompanied by an increase in solvent power for phenol, the partition-coefficient rising to about 12. In the case of certain precipitated proteins, e.g. casein, edestin, gliadin, gelatin and its derivatives, with ascending phenol concentration the coefficient of 12, however, continues to increase, thus indicating a further deviation from the partition law, but with precipitated serum albumin, egg-albumin, and pseudo-globulin the partition ratio of 12 remains constant with further increase in concentration. This is also true in the case of heat-coagulae. Gelatin, however, is precipitated so gradually and over so wide a range of phenol concentration that this in its self may be the explanation of the progressive increase in the partition-coefficient. Nevertheless it is of interest that the phenol concentration in the aqueous phase is directly proportional to the square root of the concentration in the protein phase. The results with casein, gliadin, and edestin, however, are consistent with the view that phenol and cresol become *associated* when dissolved in the precipitated proteins. Thus, when phenol or cresol is dis-

tributed between the solvents, water and benzene, the partition-coefficient $\frac{\text{Concentration of phenol in benzene}}{\text{Concentration of phenol in water}}$ is not constant, but increases with rising phenol concentration, just as is observed with certain precipitated proteins. This apparent deviation from the partition law is due to the association of phenol molecules in the benzene. Phenol, on the other hand, dissolved in a hydroxy-solvent, such as water, consists of simple molecules. Consequently the concentration of phenol in the water phase is no longer directly proportional to the concentration in the associating phase, but to some root of this figure.

As resorcinol is unassociated in benzene, a consideration of the results obtained from a study of the distribution of this dihydroxy phenol between water and gelatin is of some interest.

The Distribution of Resorcinol between Gelatin and Water

Distribution experiments described in the present paper have so far been confined to phenol itself, which on account of its limited solubility, can not be investigated at concentrations above about 7%. Additional experiments have therefore been carried out employing resorcinol in concentrations up to 20%. Like phenol it is a protein precipitant but in conformity with its lower bactericidal power, the precipitating concentration is considerably higher[1].

Estimation of resorcinol

A method similar to that employed for phenol estimation was found to give accurate results.

A volume of concentrated HCl equal to one third the volume of the resorcinol and hypobromite together, is added to the sample. Excess of N/10 sodium hypobromite is run in from the burette, and after the addition of KI, titrated with N/20 sodium thiosulphate and starch. For 10 c.c. of 0.5% resorcinol 40 cc of hypobromite and 4 cc of 20% KI are used and corresponding proportions for other quantities of resorcinol.

The following estimations were carried out with accurately known resorcinol solutions, each made up separately with resorcinol recrystallised from hot benzene.

1. 10 cc 0.100% resorcinol and 6 cc conc. hydrochloric acid required—

8 cc hypobromite	= 0.0602 gm Br
4.15 cc thio.	= 0.0166 gm Br
	0.0436
% resorcinol	= 0.01000 × 10
	0.100%

2. 10 cc 0.300% resorcinol and 11 cc of acid required—

24 cc hypobromite	= 0.1805 gm Br
12.45 cc thio.	= 0.0497
	0.1308
% resorcinol	= 0.03000 × 10 = 0.300%

[1] Cooper: Biochem. J., 7, 175-196 (1913).

3. 10 cc 0.500% resorcinol and 17 cc acid required—

40 cc hypobromite	0.3008 gm Br
20.8 cc thio.	0.0830
	0.2178
% resorcinol	0.04997 × 10
	0.500%

Distribution Experiment A—without Dialysers

TABLE XXI

1 gm gelatin : 50cc resorcinal

Blank 10 cc hypobromite alone 21.9 cc thiosulphate

With 10 cc extract 21.7 cc

0.2 cc

	Resorcinol conc. Initial	Final	Resorcinol in 1 gm gelatin	State of protein	Distribution Ratio	
	gm/100cc		gm			
(1)	0.492	0.462	0.015		3.2	
(2)	0.871	0.812	0.0295		3.6	
(3)	2.155	1.995	0.08		4.0	Mean
(4)	4.31	3.93	0.19		4.8	4.06
(5)	9.90	9.05	0.425	ppte.	4.7	
(6)	19.77	18.76	0.505	ppte.	2.7	

The analyses were carried out after three days except in (5) and (6) where six days were allowed for equilibrium. It is evident that with resorcinol, unlike phenol, precipitation of the protein is not accompanied by an increase in the distribution ratio. In (6) the gelatin had become semi-liquid and was possibly beginning to dissolve. The experiment was therefore repeated using viscose dialysers.

Distribution Experiment B—with Viscose Dialysers

(1) and (2) were analysed after two days and again after five days. (3) was analysed after four and after eight days; (4) was complete in 10 days. The results of the second analyses are shown in brackets beside those of the first.

It is seen that over a wide range of concentration the partition-coefficient averages 4. Resorcinol is thus about twice as soluble as phenol in unprecipitated gelatin, although previous investigations have shown resorcinol to be considerably the weaker germicide and protein precipitant. The bactericidal action of the phenols is thus not merely determined by their actual solubility in proteins, but is apparently due to a subsequent action on the colloidal structure of the bacterial cell.

TABLE XXII

Inside dialyser 1 gm gelatin and 20 cc resorcinol solution
Outside " 30 cc resorcinol solution.
Blank 10 cc hypobromite alone 18.2 cc thiosulphate
With 10 cc extract 18.0 cc

	Resorcinol conc. Initial gm/100 cc	Final	0.2 cc Resorcinol in 1 gm gelatin gm	State of protein	Distribution Ratio	
(1R)	0.568	0.570	0.026		4.56	
(1)	1.000	0.946 (.946)	0.027		2.85	
(2R)	2.80	2.89	0.125		4.3	Mean
(2)	5.00	4.66 (4.62)	0.715	Ppte.	3.68	3.82
(3R)	5.54	5.91	0.200	"	3.38	
(3)	10.00	9.23 (9.30)	0.385	"	4.17	
(4)	20.00	19.10 (19.10)	0.45	"	2.36	
	19.77	18.30 (18.75)	0.735	"	4.0	

The results are also of interest insomuch as, although gelatin is precipitated by resorcinol at 5% concentration, the partition-coefficient does not rise with further increase in concentration, which suggests that the resorcinol dissolved in precipitated gelatin consists of simple molecules, as is the case in benzene.

Although there is thus evidence supporting the view that *phenol* is "associated" in certain proteins, there are difficulties in the way of accepting association as the only factor responsible for the increased solvent power for phenol when a protein is coagulated. Thus, in the case of albumins and globulins coagulated by phenol or heat, when precipitation is complete, the partition-coefficient remains constant at the higher figure of 12 with further rise in phenol concentration. If the phenol were associated in the coagula, the coefficient would be expected to continue to increase as is actually the case with casein and edestin. Furthermore, when phenol is distributed between water and desamino-gelatin, the distribution-ratio also rises with ascending phenol concentration, although this protein contains OH instead of NH_2 groups, and should therefore exert a dissociative action, like water, on the phenol molecular-complexes.

Further research is necessary in order to correlate the two sets of results. It may be concluded however at the present stage that, as the partition law holds in the case of dispersed proteins, the germicidal action of phenol is due not to its molecular association within the emulsoid particles of the bacterial proteins, but rather to its capacity to induce a de-emulsification or precipitation of their colloidal solutions, or probably of one protein in particular, analogous to serum pseude-globulin, which is precipitated by very low phenol concentrations, of the same order as are known to exert bactericidal action.

The University,
Birmingham,
England.
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SOCIÉTÉ DE CHIMIE INDUSTRIELLE
28, Rue St-Dominique
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THE MECHANISM OF THE ABSORPTION OF WATER BY RUBBER

BY H. H. LOWRY AND G. T. KOHMAN

Rubber compounds as used for purposes of insulation are similar to other substances used for these purposes in that their electrical properties depend to a very great extent upon small amounts of water which are absorbed from the surroundings. In order to make an intelligent attempt to develop an insulating compound from rubber having the best possible insulating properties, it is necessary to have a knowledge of the mechanism by which water is taken up by rubber.

The data in the literature concerning the absorption of water by rubber are incomplete, and the experimental work in general was apparently not planned with the object of throwing light upon the mechanism of water absorption. In most cases the experiments were not carried far enough to enable equilibrium conditions to be predicted and in some cases rates of absorption have been assumed to be proportional to amounts of water absorbed at equilibrium, which, as will be shown, is not always true. Some investigators have studied the absorption of water resulting from contact with pure water only, in which case only information concerning rates can be obtained for a reason which will be made clear later. In order to obtain information concerning the mechanism of water absorption the relations between this process and the following factors were studied:

1. Vapor pressure of water external to the rubber.
2. Water-soluble constituents of the rubber.
3. State of the water external to the rubber (liquid and vapor).
4. Combined sulphur content of the rubber (rigidity).
5. Temperature.
6. Hydrostatic pressure upon the rubber compound.
7. Aging of rubber compounds before and during the process of water absorption.

A number of investigators have observed that rubber compounds absorb appreciable quantities of water and some have investigated the influence of some of the factors dealt with in this paper. It was observed by Hancock[1] in 1876 that a rubber bag filled with 12 ounces of water became empty after a period of thirty years. DeVries[2] and Whitby[3] observed that the water content of raw rubber varied with the humidity of the atmosphere in which it was stored. Van Rossem[4] and his co-workers, Miss van de Leur and Dekker, have shown that the amount of water absorbed by rubber compounds depends upon the humidity, temperature, and also the amount of water soluble impurities in the rubber. Obach[5] has studied the absorption of water by

[1] Weber: "The Chemistry of India Rubber," page 13 (1902).
[2] "Estate Rubber", page 602 (1920).
[3] J. Soc. Chem. Ind., **37**, 278 (1918).
[4] Kolloidchem. Beihefte, **10**, 43 (1918).
[5] "Cantor Lectures on Gutta Percha", Appendix VIII, p. 100 (1898).

rubber and gutta percha from both fresh water and sea water. He presents data which show that not only do these compounds absorb much less water from sea water than from fresh water, but that the behavior is different in other respects. In fresh water these compounds continue to gain weight even after very long periods of immersion but in sea water they either reach a constant weight or begin losing weight after comparatively short periods of immerson. Whitby[1] has shown that the moisture retaining capacity of raw rubber is closely related to the presence of serum solids which are hygroscopic. Andrews and Johnston[2] have developed a formula based upon Fick's law of diffusion which is applicable under certain conditions to the rate of absorption of water by rubber compounds. Kirchhof[3] has shown that the amount of water absorbed by rubber depends upon the acidity of the rubber and also upon the period of vulcanization. Boggs and Blake[4] have recently published a paper on the effect of various factors upon the rate of absorption of water by rubber. In a more recent paper Williams and Kemp[5] discuss the effect of absorbed water on the electrical properties of submarine insulation.

In order definitely to determine the mechanism of water absorption by rubber, a comprehensive study of the process was made, the results of which follow. In making the study it was deemed advisable to eliminate as many complicating factors as possible. The compounds used in the study were therefore in most cases simple rubber sulphur compounds.[6] To prevent "blooming" of sulphur and consequently changes in weight and composition of the sheet, the period of vulcanization was so regulated that the free sulphur content in most cases was less than one per cent. Certain of the compounds were therefore somewhat over cured.

Experimental Procedure

The method of attacking the problem was to make a study of the various factors which influence the amount and rate of absorption of water. The absorption of water was followed by three methods.

1. In most cases test specimens fifty mils in thickness and two inches on a side were prepared. These test specimens were dried in vacuum, weighed and immersed in solutions of various aqueous vapor pressures. Sodium chloride solutions were used for the most part, partly because Kahlenberg[7] showed that sodium chloride would not diffuse into rubber, and partly because in certain cases it was desired to obtain information concerning the absorption from sea water. In order to reduce evaporation of the solutions, the

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[1] India Rubber World, **59**, 141 (1918).

[2] J. Am. Chem. Soc., **46**, 640 (1924).

[3] Kolloid-Z., **35**, 367 (1924).

[4] J. Ind. Eng. Chem., **18**, 224 (1926).

[5] Williams and Kemp: J. Franklin Inst., **203** (1927).

[6] Many experiments not reported in this paper have shown that in general the amount of water taken up by filled rubbers, if made free from pores, can be calculated from their rubber content unless the filler itself is either water soluble or hygroscopic.

[7] J. Phys. Chem., **10**, 141 (1906).

vessels containing the test specimens immersed in solutions of equal vapor pressures were placed in a humidifier, and the solutions were changed periodically to correct for changes in concentration due to the absorption of water by the sheets. The absorption of water was followed by removing the sheets from the solution, washing free from sodium chloride, blotting carefully between sheets of hard filter paper in a standard way, transferring to a weighing bottle and weighing. They were then again immersed in the solution. The blotting and weighing was done as quickly as possible to prevent changes in the moisture content of the sheet. The humidifiers containing the samples at

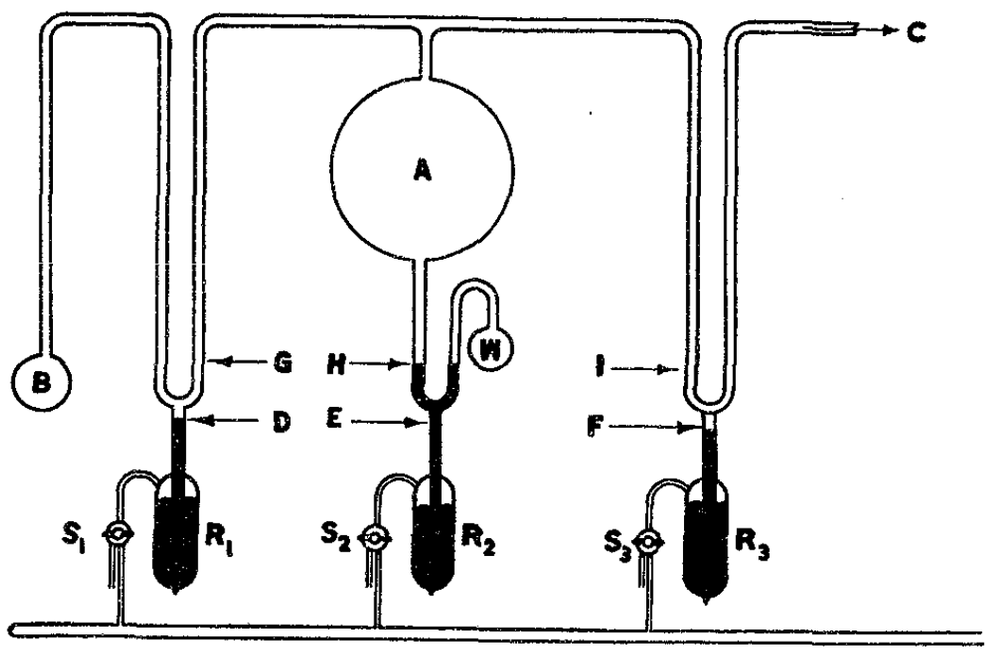


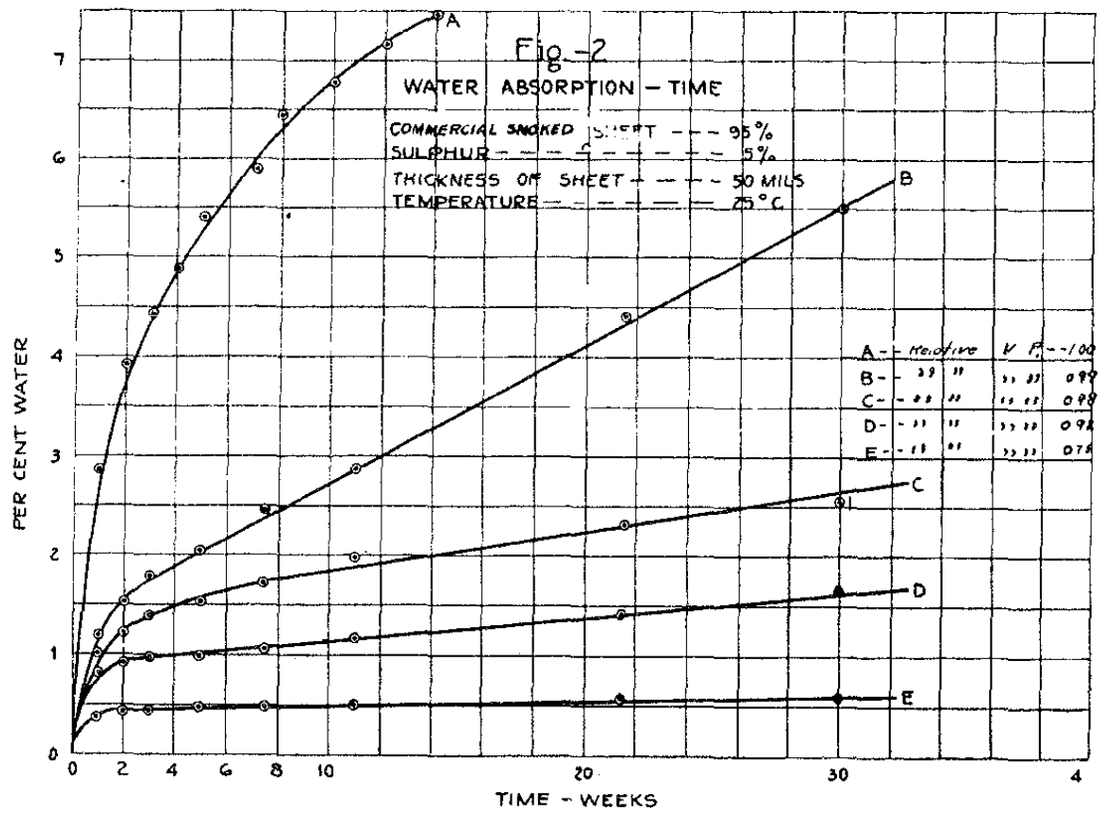
FIG. 1

25°C. were ordinarily kept in a room the temperature of which was approximately 25°C. In certain cases they were immersed in a thermostat kept at a temperature of 25° ± 0.1. At temperatures other than 25°C. they were kept in a constant temperature room the temperature of which was controlled by a thermostat to ± 1°C.

2. The absorption was followed by observing the changes in pressure of water vapor in an enclosed system of known volume containing the sample. The apparatus used, shown schematically in Figure 1, is so designed that stopcocks need not be relied upon to prevent leakage. The various systems can be closed or opened by regulating the height of the mercury columns above or below the level D E F by controlling the air pressure above the mercury in the reservoirs R_1, R_2 and R_3 by means of the two way stopcocks S_1, S_2 and S_3 which are connected to both a vacuum line and to atmospheric pressure.

The sample in the form of finely cut pieces or very thin sheets is placed in the bulb B and sealed to the apparatus. With the mercury levels at D, H and F, the sample is pumped out by means of mechanical pumps backed by a mercury diffusion pump connected to C. The mercury level of R_1 is then raised to G and that of R_3 to 1. The mercury level of R_2 is then slowly lowered

until water vapor furnished by the evaporation of the water in bulb W bubbles past the mercury into the system A. Any desired pressure of vapor can be admitted by following the difference of the mercury levels at I which serve as a manometer. These levels are read to ±0.03 mm by a micrometer gage[1] not shown. From the volume of the system A and the pressure the amount of water vapor admitted is calculated. The mercury level of R_1 is then lowered to D which allows the water vapor to come in contact with the sample. When the pressure of water vapor in the system has become constant the



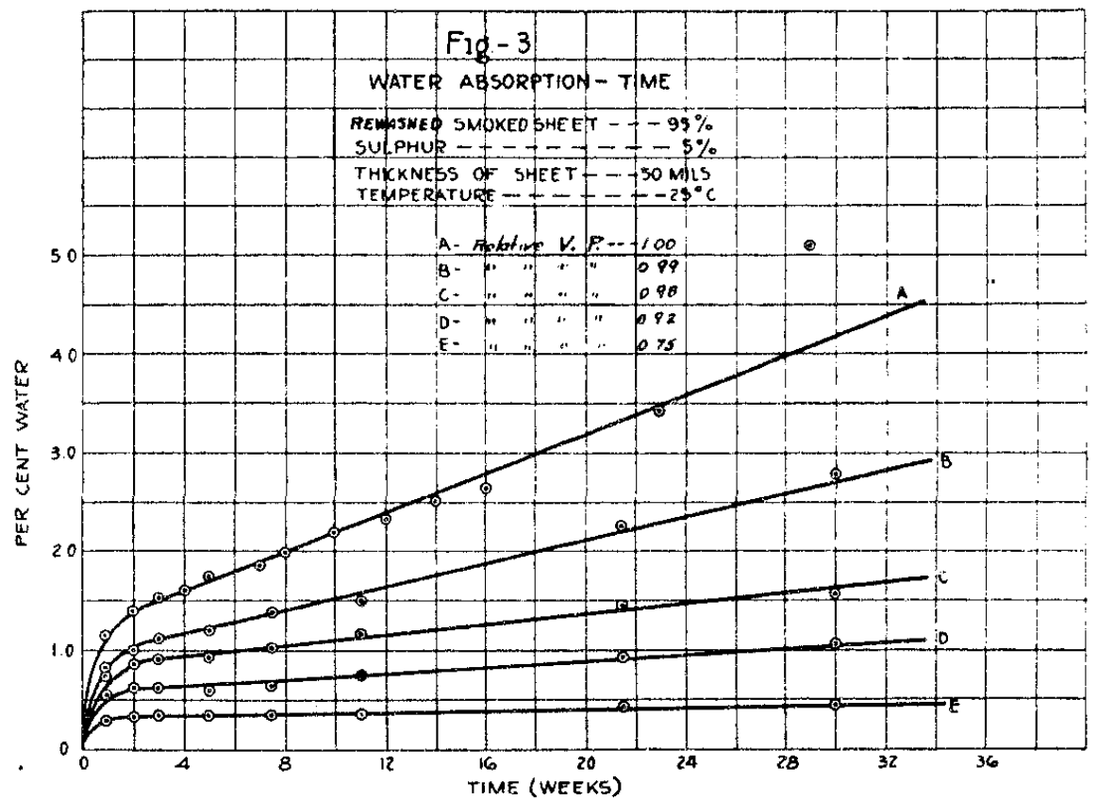
pressure is carefully read as before and the amount of water vapor remaining calculated from this pressure and the volume of system A plus that of bulb B and connecting tubing. By repeating these operations as many measurements as are desired can be obtained at pressures from zero to the vapor pressure of water at the temperature of the apparatus. The temperature of the samples was controlled in this case by immersing the bulbs containing the samples in a thermostat, the temperature of which was kept at the specified temperature ±0.2°C.

3. A method similar to that used by Miss van de Leur[2] was used in order to obtain equilibrium values rapidly. The samples in the form of thin sheets or finely cut pieces in weighing bottles were exposed to water vapor above solutions of known vapor pressure until constant weight had been reached. It was found necessary, in order to prevent oxidation of the samples, to use containers which could be pumped free from air after each weighing of samples.

[1] Ferguson: J. Wash. Acad. Sci., **10**, 285 (1920).

[2] Kolloidchem. Beihefte, **10**, 45 (1918).

The joints of the containers were then sealed with a beeswax-rosin mixture containing 20% rosin. At high relative vapor pressures, (P/P_o where P is the vapor pressure of water over the solution and P_o that of pure water), the method was found to be unsatisfactory because of the condensation of moisture on the weighing bottles. The temperature control in this case was the same as that described under method I.



Experimental Results

In Table I A-E are given the average percent weight gains of sheets of various combined sulphur contents after the specified time intervals of immersion in salt solutions of various vapor pressures. The vapor pressures given in the tables are those of the solutions at 25°C. A more complete description of the compounds used is given in Table I F. The data were obtained by method I. The humidifiers in which the sheets were kept were not kept free from air.

In Figs. 2 and 3 the results for sheets No. 5 and 10 of Table I A-E are plotted. The results for the other sheets fall on similar curves. If the water content of each sheet at the end of 210 days be plotted against vapor pressure of the solution in which the sheet was immersed curves of the type shown in Figure 4 are obtained.

There are no experimental determinations on the portions of the curves of Fig. 4 below 18 m.m. because vapor pressures of sodium chloride solutions at 25°C have a lower limit of 17.9 m.m., that being the vapor pressure of a saturated sodium chloride solution. In order to investigate this portion of the curve and also to determine whether or not the vapor pressure of water external to the rubber is the factor which causes the amount of water absorbed

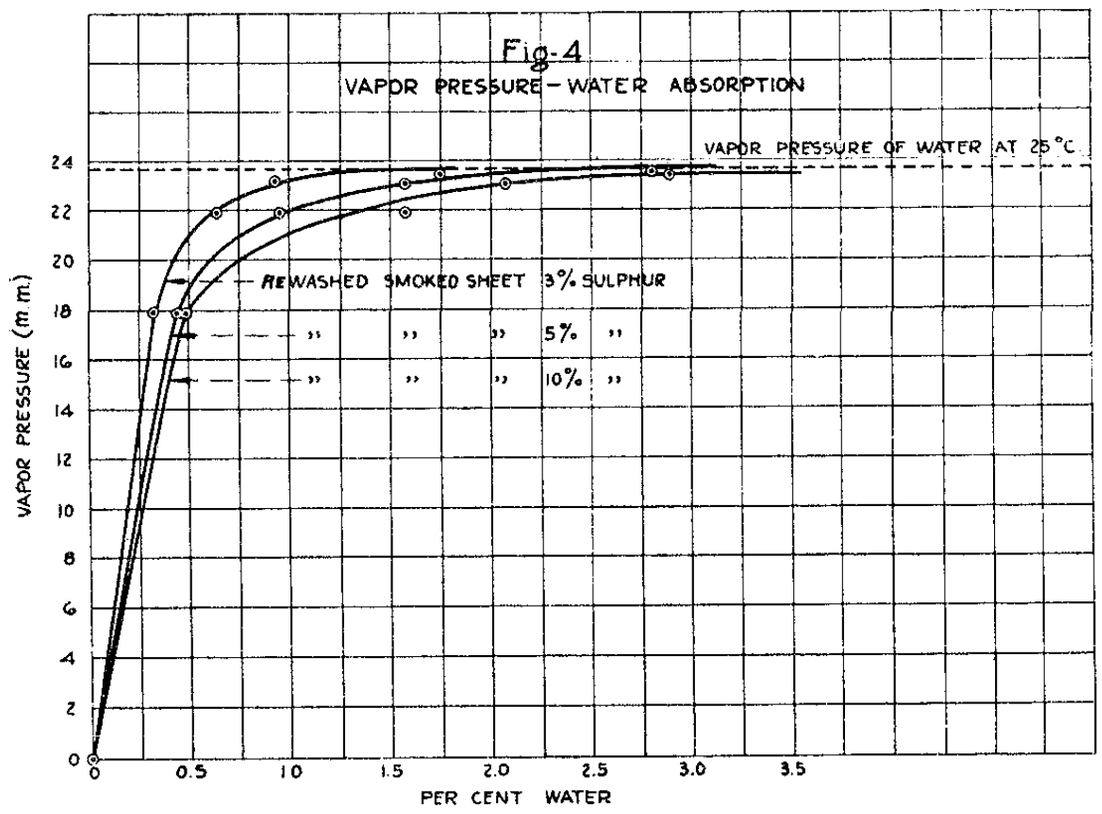


TABLE I

Mean Percentage Gain in Weight of Rubber Sheets Immersed in Water and in Salt Solutions

A

Distilled Water, Vapor Pressure—23.6 m.m.

Time (days)	Rewashed Smoked Sheet Sheet No.				Commercial Smoked Sheet Sheet No.			
	1	2	3	4	5	6	7	8
7	1.14	0.51	0.10	0.23	2.86	1.53	0.49	0.30
14	1.39	0.69	0.20	0.28	3.91	2.05	0.69	0.34
21	1.52	0.84	0.24	0.26	4.44	2.40	0.86	0.29
28	1.60	——	0.29	——	4.88	2.59	——	——
35	1.75	1.07	0.37	——	5.40	2.89	0.95	——
49	1.86	1.37	0.40	——	5.90	3.23	1.06	——
56	2.00	1.51	0.47	——	6.47	3.49	1.09	——
70	2.21	1.61	0.44	——	6.78	3.71	1.15	——
84	2.33	1.74	0.46	——	7.18	3.92	1.17	——
98	2.51	1.79	0.48	——	7.49	4.11	1.19	——
112	2.66	——	0.49	——	7.80	4.32	——	——
160	3.45	2.33	——	——	8.81	5.44	1.26	——
200	3.14	2.49	0.54	——	9.62	6.55	1.27	——
260	7.38	2.82	0.59	0.36	10.68	7.73	1.40	0.48
440	12.45	3.75	0.76	0.40	14.70	15.30	2.08	0.51

B

1.0% Sodium Chloride Solution, Vapor Pressure—23.5 m.m.

Time (days)	Rewashed Smoked Sheet Sheet No. 9	10	11	12	13	Commerical Smoked Sheet Sheet No. 14	15	16	17	18
7	0.91	0.82	0.51	0.29	0.23	1.52	1.18	0.99	0.34	0.29
10	——	——	0.68	0.32	0.26	——	——	1.19	0.41	0.31
14	0.19	1.00	0.70	0.38	0.28	1.95	1.52	1.43	0.47	0.35
21	1.28	1.12	0.77	0.41	0.28	2.24	1.78	1.65	0.51	0.35
35	1.28	1.18	0.86	0.48	0.29	2.55	2.03	1.94	0.61	0.39
52	1.39	1.37	1.11	0.60	0.36	2.96	2.46	2.34	0.72	0.43
77	1.50	1.51	1.32	0.63	0.33	3.27	2.87	2.70	0.78	0.42
105	——	——	1.76	0.74	0.37	——	——	3.09	0.90	0.47
150	1.59	2.28	2.11	0.82	0.37	4.04	4.43	3.43	0.95	0.46
210	1.74	2.80	2.86	1.04	0.37	4.61	5.53	4.17	1.15	0.47
290	——	——	3.58	1.45	0.37	——	——	5.05	1.48	0.47

C

3.5% Sodium Chloride Solution, Vapor Pressure—23.1 m.m.

Time	Rewashed Smoked Sheet Sheet No. 9	10	11	12	13	Commerical Smoked Sheet Sheet No. 14	15	16	17	18
7	0.81	0.74	0.50	0.27	0.22	1.29	1.01	0.92	0.31	0.27
10	——	——	0.68	0.31	0.25	——	——	1.12	0.38	0.31
14	0.87	0.86	0.71	0.38	0.26	1.56	1.24	1.27	0.44	0.34
21	0.92	0.91	0.74	0.40	0.26	1.77	1.40	1.44	0.48	0.35
35	0.86	0.92	0.86	0.45	0.31	1.86	1.51	1.65	0.61	0.38
52	0.93	1.02	1.00	0.54	0.31	2.02	1.71	1.99	0.70	0.41
77	0.93	1.19	1.15	0.57	0.31	2.17	1.97	2.17	0.70	0.40
105	——	——	1.30	0.67	0.31	——	——	2.55	0.81	0.41
150	0.93	1.46	1.64	0.76	0.35	2.30	2.31	2.71	0.90	0.45
210	0.79	1.58	2.08	0.95	0.35	2.26	2.56	3.13	1.09	0.45
290	——	——	2.84	1.19	0.41	——	——	3.61	1.34	0.53

D

10.0% Sodium Chloride Solution, Vapor Pressure—21.9 m.m.

Time (days)	Rewashed Smoked Sheet Sheet No. 9	10	11	12	13	Commerical Smoked Sheet Sheet No. 14	15	16	17	18
7	0.51	0.54	0.45	0.24	0.22	0.95	0.80	0.78	0.30	0.23
10	——	——	0.52	0.30	0.27	——	——	0.90	0.37	0.32
14	0.59	0.62	0.54	0.35	0.27	1.03	0.91	0.99	0.41	0.32
21	0.55	0.61	0.57	0.87	0.27	1.08	0.96	1.12	0.44	0.32
35	0.52	0.58	0.66	0.38	0.30	1.05	0.96	1.26	0.52	0.37
52	0.54	0.64	0.80	0.49	0.36	1.09	1.04	1.37	0.62	0.41
77	0.64	0.75	0.85	0.51	0.30	1.09	1.15	1.43	0.62	0.38
105	——	——	0.98	0.57	0.33	——	——	1.51	0.68	0.40
150	0.64	0.94	1.12	0.65	0.35	1.22	1.42	1.64	0.72	0.41
210	0.64	1.09	1.57	0.74	0.35	1.25	1.67	1.75	0.82	0.43
290	——	——	1.82	0.88	0.38	——	——	2.01	0.94	0.46

E

Saturated Sodium Chloride Solution, Vapor Pressure—17.9 m.m.

Time (days)	Rewashed Smoked Sheet Sheet No. 9	10	11	12	13	Commerical Smoked Sheet Sheet No. 14	15	16	17	18
7	0.29	0.28	0.31	0.21	0.19	0.39	0.38	0.44	0.22	0.21
10	——	——	0.33	0.22	0.21	——	——	0.50	0.23	0.24
14	0.30	0.33	0.33	0.25	0.22	0.45	0.43	0.50	0.26	0.24
21	0.30	0.34	0.33	0.25	0.22	0.45	0.43	0.50	0.26	0.24
35	0.30	0.34	0.34	0.27	0.22	0.42	0.46	0.53	0.33	0.27
52	0.30	0.34	0.39	0.33	0.27	0.42	0.46	0.54	0.36	0.31
77	0.32	0.35	0.42	0.31	0.25	0.45	0.49	0.57	0.36	0.28
105	——	——	0.48	0.34	0.25	——	——	0.60	0.38	0.31
150	0.32	0.43	0.48	0.34	0.25	0.48	0.57	0.61	0.41	0.31
210	0.33	0.45	0.48	0.34	0.25	0.48	0.59	0.61	0.41	0.31
290	——	——	0.60	0.37	0.25	——	——	0.68	0.43	0.31

F

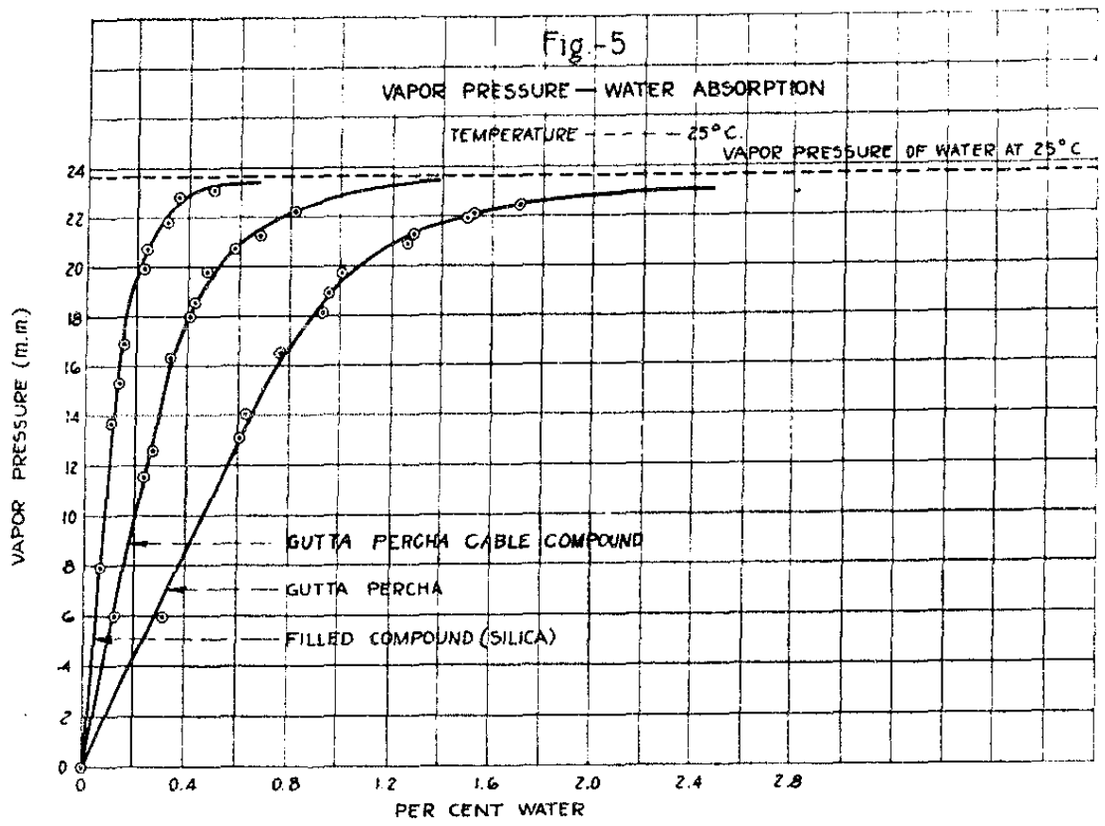
Description of Sheets Numbers 1 to 18 inc.

Sheet No.	Rubber	Cure at 50 lbs. Steam Pressure Rise	Cure (hrs.)	Total S. %	Free S.** %
1	Rewashed* S. S.	15′	3	5	1.31
2	" " "	30′	7	10	0.18
3	" " "	1 hr.	10	20	0.18
4	" " "	2 hr.	14	30	0.44
5	Commercial S. S.	15′	3	5	0.75
6	" " "	30′	7	10	0.50
7	" " "	1 hr.	10	20	0.12
8	" " "	2 hr.	14	30	0.46
9	Rewashed S. S.	10′	3⅓	3	1.13
10	" " "	15′	5	5	0.56
11	" " "	30′	7	10	0.18
12	" " "	1 hr.	10	20	0.12
13	" " "	2 hr.	14	30	0.48
14	Commercial S. S.	10′	3⅓	3	0.39
15	" " "	15′	5	5	0.14
16	" " "	30′	7	10	0.11
17	" " "	1 hr.	10	20	0.13
18	" " "	2 hr.	14	30	0.95

* The rewashed rubber used in these experiments was washed by a special process developed to remove the water soluble constituents from rubber with a minimum amount of physical deterioration. Prior to washing the rubber is passed through a creping mill for 18 minutes during which time it is subjected to a spray of water ranging in temperature between 43 and 52°C. The creped rubber is then washed on a Werner and Pfleiderer washing machine and subjected to a spray of water the temperature of which is lowered from 65 to 45°C during the process. After wahsing the rubber is again creped to uniform thickness and dried in vacuum.

** In order to reduce the free sulphur content to these values the compounds in some cases were badly over-cured. It was necessary, however, to keep it below approximately one per cent, (the solubility of sulphur in rubber at room temperature) to prevent blooming which would make it impossible to follow the absorption of water by weighing the sample.

by sheets immersed in sodium chloride solutions to decrease as the salt concentration increases, method 2, which enables the absorption to be studied over the entire vapor pressure range, was developed. In Table II the amounts of water absorbed at equilibrium by various samples of rubber as determined by this method are given. The results fall also on curves of the type of that in Fig. 4 as is shown by Fig. 5. Wilson and Fuwa[1] have discussed briefly various types of curves showing the relation between vapor pressure and



amount of water absorbed. The character of the curves such as are shown in Fig. 5 together with other results which will be discussed later have led to a theory of the mechanism of the absorption of water by rubber which has been found to be in harmony with all of the observations concerning this process that have come to the attention of the writers. This theory will be discussed now in order that it may be of help in explaining the results of further experimentation.

It will be observed from Fig. 5 that the solubility of water in rubber at vapor pressures below approximately 16 m.m. at 25° is directly proportional to the first power of the pressure. At these pressures then the solubility obeys Henry's Law and therefore it is probable that the water and rubber form a true solution. Other facts as well point to this conclusion. For example, as is shown by the data plotted in Figs. 2 and 3, the soluble impurities in the rubber do not affect the amount of water absorbed at low vapor pressures appreciably. The sheets from which the soluble impurities have been re-

[1] J. Ind. Eng. Chem., **14**, 913 (1922).

moved by washing absorb very nearly as much water as the sheets of commercial rubber at a vapor pressure of 17.9 m.m. while at higher pressures the

TABLE II

% Water absorbed at Equilibrium by Rubber Sheets
as determined by Method 2

Temp. = 25°C.
P = Pressure of water vapor in equilibrium with the samples.

	Compound Numbers				
P(m.m.)	VII	VIII	IX	X	XI
3	0.06	0.07	0.05	0.06	0.03
5	0.10	0.11	0.08	0.10	0.07
10	0.19	0.24	0.16	0.21	0.16
15	0.28	0.36	0.24	0.31	0.23
18	0.47	0.52	0.28	0.41	0.29
20	0.78	0.78	2.46	0.52	0.33
22	1.58	1.30	3.30	0.77	0.45
23	2.50	2.16	4.50	1.07	0.60
23.2	2.80	2.50	8.0	1.16	0.75
P(m.m.)	XII	XIII	XIV	XV	XVI
3	0.05	0.04	0.04	0.15	0.03
5	0.10	0.06	0.06	0.23	0.04
10	0.23	0.11	0.13	0.47	0.09
15	0.38	0.17	0.19	0.68	0.14
18	0.60	0.27	0.28	0.88	0.16
20	0.88	0.45	0.41	1.21	0.21
22	1.68	0.76	0.63	1.53	0.30
23	2.95	1.20	0.94	2.16	0.41
23.2	4.75	1.40	1.06	——	0.52

Description of Compounds of Table II

Compound No.	Description of Compound
VII	Commercial smoked sheet, 4.25% combined sulphur, 0.75% free sulphur.
VIII	Commercial latex crepe, 2.61% combined sulphur, 0.39% free sulphur.
IX	Rewashed smoked sheet, 4.36% combined sulphur, 0.64% free sulphur, 0.4% sodium chloride.
X	Gutta Percha Cable Compound.
XI	Hard rubber dust, commercial smoked sheet, 23% combined sulphur.
XII	Commercial raw smoked sheet.
XIII	Washed balata.
XIV	Deresinated balata.
XV	Gutta Percha.
XVI	Filled Rubber Compound (Silica)

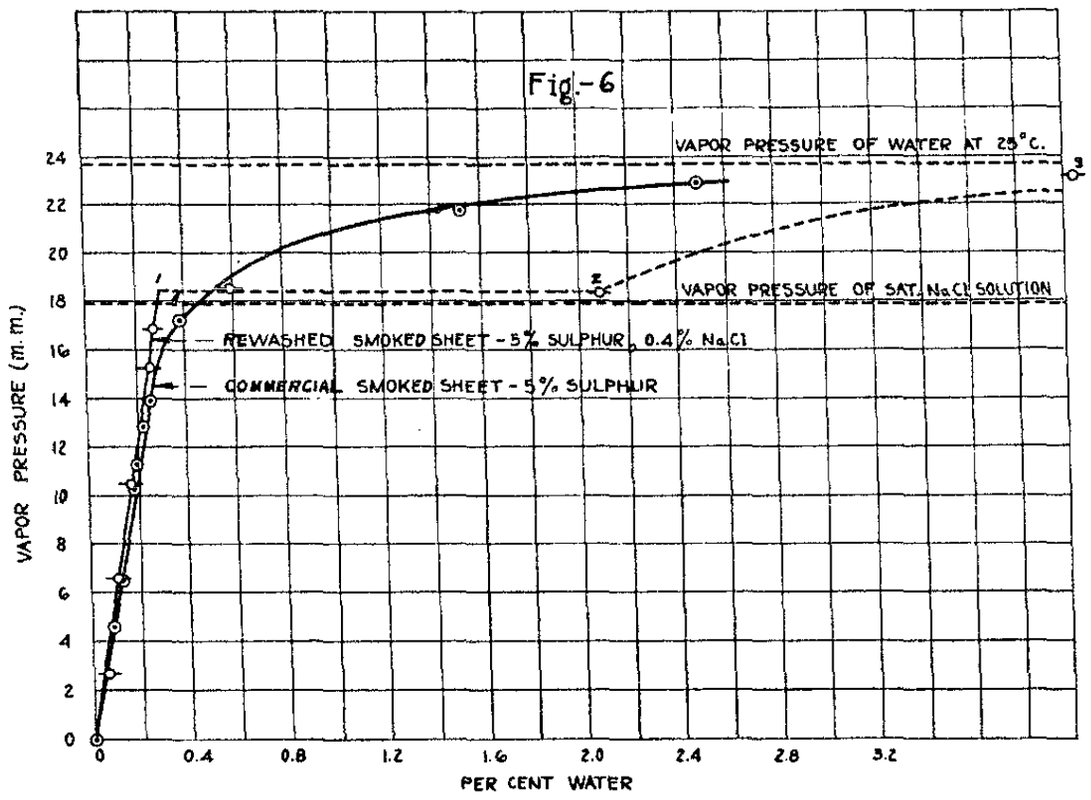
soluble impurities have a very noticeable effect. That pores in the rubber are not a factor is shown by the character of the vapor pressure curves. If pores were present in the sheets the water would enter the sheet at constant pressure until they were filled, and therefore the lower parts of the curves of Fig. 5 would deviate from unbroken straight lines. Further evidence that pores do not play a part in water absorption is the fact that rubber sheets, as will be shown later, expand in volume an amount very nearly equal to the volume of water absorbed.

Above a certain vapor pressure (approximately 16 m.m. at 25°C) the solubility no longer obeys Henry's Law but is much greater than the law would predict, and Figs. 2 and 3 show that this deviation is much greater in the case of commercial rubber than of rewashed rubber. It was, therefore, concluded that when the vapor pressure of water external to the rubber is raised slightly above that of a saturated solution of the water-soluble impurities in the rubber, water diffuses in to form such a solution and then to dilute it until the vapor pressures of the internal and external solutions are equal, the driving force being the vapor pressure difference. If these soluble impurities be washed out, the amount of water absorbed should be reduced to that actually dissolved in the rubber as a lower limit.

The fact that the solubility does not begin to deviate from Henry's Law until the vapor pressure is raised above about 16 m.m. indicates that the gross solubility of the impurities in rubber is such that the vapor pressure of a saturated solution of them is approximately 16 m.m. at 25°C. The theory would lead one to predict that a rubber compound having a single soluble salt as an impurity should show a definite break in the amount of water absorbed with change of vapor pressure or humidity, and also that the curves such as are given in Fig. 5 for compounds containing several different soluble impurities should consist of a series of steps at high relative vapor pressures if the solubility of each impurity were independent of the presence of the other impurities. The effect of one impurity upon the solubility of another, however, probably is sufficient to make the breaks indefinite and impossible of detection. In order to test the theory a compound was prepared of rewashed rubber to which 0.4% of sodium chloride had been added by milling the very finely divided salt into the rubber on a rubber mill. The sheet is identified as compound IX in Table II. The experimental determinations of the amounts of water absorbed at various vapor pressures of water are given in Table III and the absorption curve is shown in Fig. 6. It is evident that below the vapor pressure of a saturated salt solution the curve for the compound made of rewashed rubber in which sodium chloride had been milled is practically identical with that for the compound made of commercial rubber. The latter curve bends at a slightly lower vapor pressure than does the former, indicating that a small amount of a substance having a greater solubility than sodium chloride had been removed from the rubber by washing. When the vapor pressure of water external to the compound is raised slightly above that of a saturated sodium chloride solution a large amount of water enters the com-

TABLE III

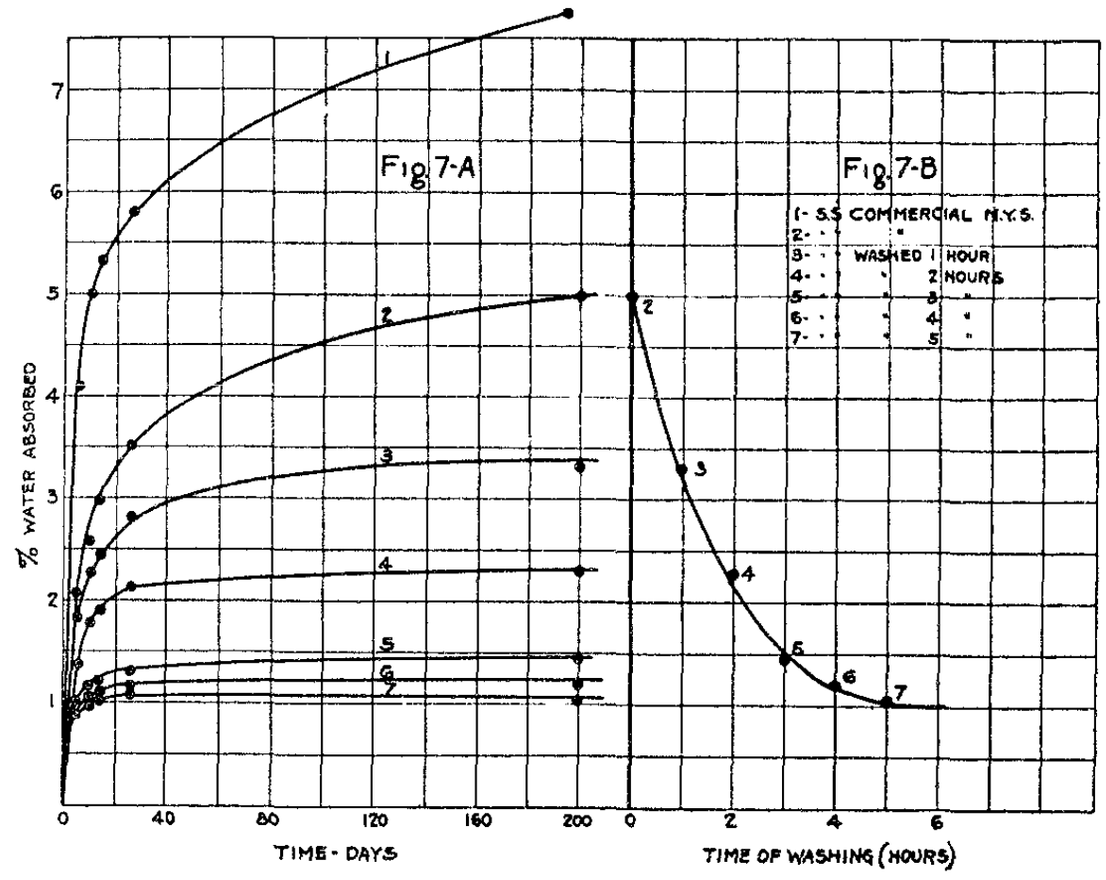
P m.m.	% Water Absorbed	P m.m.	% Water Absorbed
2.72	0.07	16.91	0.26
6.60	0.11	18.67	0.58
10.57	0.16	18.7	2.09
11.24	0.19	23.5	8.7
15.21	0.24		



pound at constant pressure causing the break in the curve shown in Fig. 6. This water enters the compound very slowly because of the small difference in vapor pressure of the water internal to the compound and that external to it. This difference in pressure is the driving force causing the water to enter the compound. Although the sample was cut in very small pieces a period of four weeks was required for point 2 to be reached. After point 2 has been reached and all of the salt in the compound is in solution, water ceases to enter the sheet until the pressure of water vapor external to the sheet is increased above that of a saturated sodium chloride solution. As the external pressure is increased water will enter the sheet and dilute the internal solution until the vapor pressure of water from this solution is equal to the external pressure.

In order to further check the theory and to determine the feasibility of reducing the amount of water absorbed by rubber compounds by subjecting them to a washing process a sample of raw smoked sheet was washed for periods of from one to five hours. Samples of the rubber were taken at the

end of each hour period of washing and made into 50 mil sheets for water absorption studies. The experimental results presented in table No. 4 are shown graphically in Fig. 7 A. In Fig. 7 B the amount of water absorbed at the end of 200 days is plotted against the time of washing. The results clearly show that the amount of water absorbed decreases with the length of the period of washing.



The water soluble matter in these samples was also determined by a method which is essentially that described by A. van Rossem.[1] Five grams of rubber were cut in small pieces and placed in a pyrex glass extraction apparatus of the type described by T. B. Ford.[2] The sample was covered with 100 c.c. of distilled water and the apparatus placed on a hot plate regulated to keep the water boiling gently. After a period of eight hours the solution was decanted from the sample, filtered and set aside. The rubber was further extracted with 100 c.c. distilled water in a similar manner for a period of sixteen hours. The solution was again decanted from the sample, filtered and added to the first extract. The combined filtrates were then evaporated to approximately 25 c.c., transferred, together with any solid which had separated, to a platinum dish and evaporated to dryness at 100°C. The residue was then heated to 100°C. until its weight remained constant. In order to correct for the solubility of the glass, blanks were run in an exactly similar manner.

[1] Comm. Delft. **2**, 406 (1917); Chem. Abs., **12**, 639 (1918).
[2] J. Am. Chem. Soc., **34**, 552 (1912).

Because of the small amounts of material to be extracted the errors in the determinations are large. The results, however, tabulated in Table IV and plotted in Fig. 8 show that the amount of soluble material extracted decreases with length of the washing period from 0.225% to approximately 0.05%. The results tabulated in Table IV and those plotted in Figs. 7 and 8 show also that the sample of unwashed rubber having a high water-soluble content absorbs much more water than do any of the other samples.

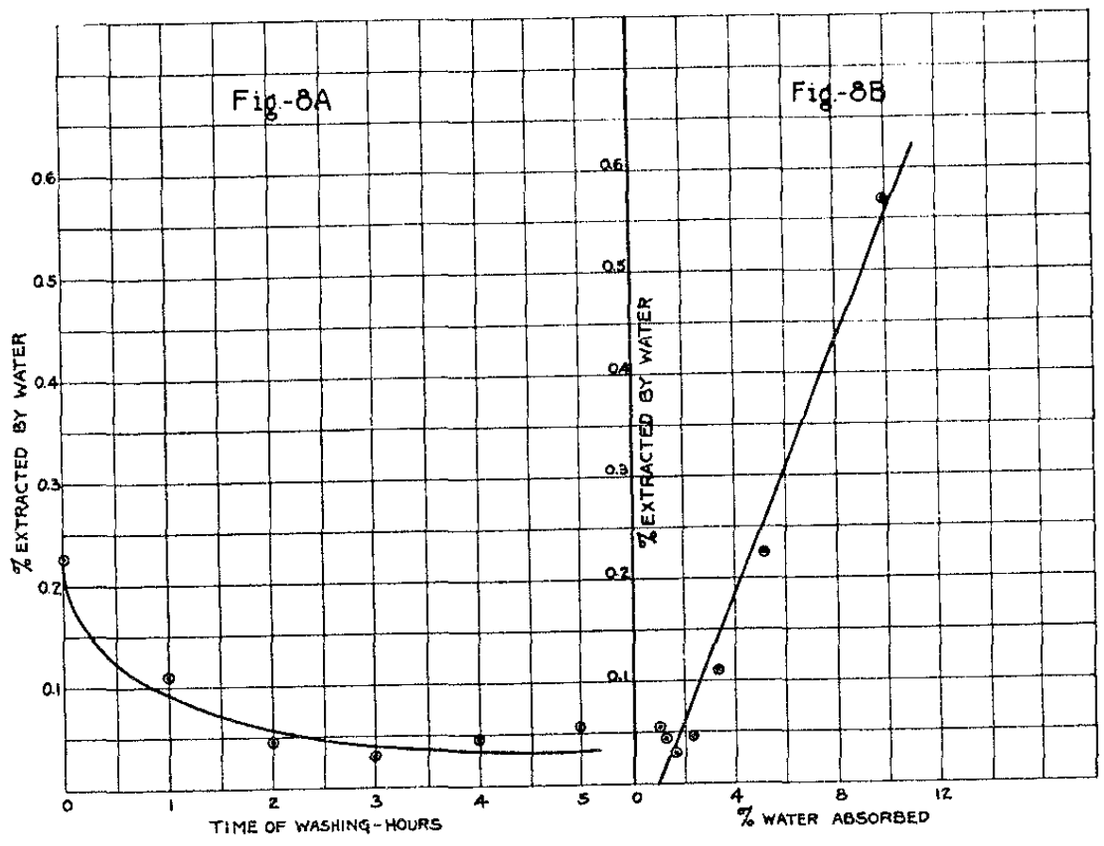


TABLE IV

Relation between Water Absorption and Water-Soluble Content of Raw Rubber

Description of Samples	% Water Absorbed; P/P_o = 0.98					% Extracted By Water
	5 (days)	10	14	26	200	
Commercial S. S. (Lot 1)	4.10	5.00	5.30	5.80	8.00	0.574
Commercial S. S. (Lot 2)	2.05	2.56	2.97	3.47	5.00	0.225
S. S. Lot 2 Washed one hour.	1.83	2.24	2.44	2.81	3.30	0.110
S. S. Lot 2 Washed two hours.	1.37	1.77	1.89	2.12	2.30	0.045
S. S. Lot 2 Washed three hours.	1.00	1.16	1.21	1.30	1.45	0.030
S. S. Lot 2 Washed four hours.	0.91	1.05	1.10	1.15	1.18	0.045
S. S. Lot 2 Washed five hours.	0.88	0.99	1.03	1.07	1.07	0.057

It will be noted that there is evidence of a minimum in the graph of Fig. 8 A. The deviations of the points from the curve as drawn are probably within the experimental error, but it is possible that the minimum is real. As the time of washing increases, the tackiness of the rubber increases markedly. Some of the rubber constituents may be redispersed by the long period of extraction and the amount dispersed would naturally increase with the tackiness. An examination of the residue from the extractions indicated the presence of small amounts of rubber. After the extraction has been carried to a certain stage the value of the water extract, as determined above, may therefore reach a minimum value and begin to increase with time of washing even though the amount of water absorbed may decrease continuously.

If equilibrium values be estimated from the curves of Fig. 7 A and plotted against the water extract, the points fall roughly on a straight line as is shown in Fig. 8 B. This straight line, however, does not pass through the origin but indicates that when all of the soluble material is removed from the rubber approximately one percent of water will still be absorbed. This then may be regarded as further evidence that the absorption of water consists of two processes.

The theory as stated would lead one to predict that the absorption of water by sheets of rubber immersed in a solution will be the same as by the same sheets suspended in an atmosphere having a pressure of water vapor equal to the vapor pressure of the solution. In order to confirm this prediction and also to learn whether or not results obtained by the three methods used to follow the absorption are comparable, the absorption of water by sheets of a rubber compound immersed in a 3.5% sodium chloride solution and sheets suspended in the vapor above the same solution was studied. Ten sheets of the following composition:

Commercial Smoked Sheet	95.0%
Combined Sulphur	4.25%
Free Sulphur	0.75%

were immersed in the solution contained in a vacuum humidifier and ten suspended in the vapor above the solution. The humidifier was pumped free from air, sealed with the beeswax-rosin mixture and immersed in a thermostat at 25°C. The humidifier was opened periodically and the sheets weighed. The results of the experiment given in Table V show that both the rate and the amount of absorption are very nearly the same in both cases. The sheets in the vapor apparently contain about 0.25% less water than those in the solution over the entire period. It is believed that this difference represents a surface film which is not removed by the blotting operation in the case of sheets immersed in the solution. The difference between the weights of sheets A and B in Table V becomes slightly less with time, but this may well be due to the extraction of certain constituents of the rubber by the water.

Unless precautions are taken to ensure that the temperature of the sheets in the vapor is the same as that of the sheets in the solution and that the rate of evaporation of the solution is great enough to always keep the surfaces of

the sheets saturated, the results will not be the same in both cases. Very slight differences will cause very great differences in water absorption, particularly at high relative vapor pressures. For example at 25°C a change of temperature of 1° changes the vapor pressure of water nearly 1.5 m.m. and at a relative vapor pressure of 0.98 a change of 1 m.m. in vapor pressure may cause a change of 1% or more in water content in the case of unwashed rubber. This probably is the answer to the question which puzzled Miss van de Leur[1]

TABLE V

Comparison of Water Absorption of Sheets A in Water Vapor and Sheets B immersed in the Solution

Days	% H_2O Mean of 10 Sheets A	% H_2O Mean of 10 Sheets B	Average Deviation from Mean A	Average Deviation from Mean B	B%−A%
6	1.11	1.32	±.05	±.03	0.21
11	1.40	1.69	.04	.03	0.29
16	1.74	1.93	.08	.02	0.19
23	1.86	2.16	.06	.02	0.30
30	2.03	2.29	.08	.03	0.26
38	2.24	2.50	.07	.05	0.26
46	2.28	2.56	.07	.03	0.28
71	2.27	2.77	.10	.03	0.50
86	2.35	2.87	.10	.03	0.52
145	2.56	2.96	.11	.05	0.40
167	2.85	3.01	.09	.05	0.16
183	2.91	3.04	.06	.06	0.13
199	3.02	3.09	.05	.05	0.07
225	3.13	3.23	.04	.06	0.10
276	3.14	3.20	.03	.05	0.06
				Average	0.25

"why does Hevea sheet in saturated vapor take up 1.85% of water and in pure water 21.5%". A rubber sheet immersed in distilled water should theoretically continue absorbing water indefinitely because the soluble impurities in the rubber sheet will prevent the vapor pressure of the water in the sheet from equaling that of pure water until infinite dilution is reached or until the pressure on the internal solution caused by the resistance of the sheet to swelling increases the vapor pressure of the internal solution sufficiently to make it equal to that of pure water. If the temperature of the sheets in the vapor were only 1°C. above that of the pure water at 25°C. the result would be the same as if the sheets were immersed in a solution of P/P_0 equal to about 0.94. The amounts of water absorbed by a rubber compound in distilled water and in a solution of P/P_0 equal to 0.94 might easily differ by more than the amount observed by Miss van de Leur.

[1] Kolloidchem. Beihefte, **10**, 45 (1918).

In certain cases, however, even though every precaution be taken to prevent temperature differences, the amount of water absorbed from the solution will be different from that absorbed from the vapor of the solution. If one of the components of the solution other than the water is soluble in the rubber compound, as will be the case in solutions of ammonia, phenol and certain acids, this compound will be distributed between the water and the rubber. The rubber samples immersed in the solution will, as a result of this distribution, absorb more water than those in the vapor. If soluble material should diffuse from the rubber compound into the solution the effect would be in the opposite direction. However, it would be expected that the amount of water absorbed by the samples immersed in the solution would increase with time to a maximum and finally decrease as the soluble material diffused into the solution.

Sulphur Content—Water Absorption

It might be expected from the theory of the mechanism of water absorption by rubber that the rigidity of a compound would have an appreciab effect upon the amount of water absorbed. Experiments in this laboratory have shown that rubber swells while absorbing water to an extent very nearly equal to the volume of water absorbed. The pressure which the rubber exerts upon the solution internal to the rubber in opposing this swelling will result in an increase in the vapor pressure of the internal solution. Obviously, then an increase in rigidity of the rubber should cause less water to be absorbed than might be expected from the amount of water soluble constituents in the material. If the sulphur during vulcanization had no action upon these water soluble constituents causing them to become insoluble the effect of rigidity could be determined by studying the relation of combined sulphur content (a factor influencing rigidity) to water absorption. The amount of water actually dissolved in the rubber hydrocarbon when exposed to pressures of water vapor below 98% of that of pure water is probably less than one per cent as determined by extending the straight part of the vapor pressure curves and by washing experiments. Therefore the greater part of the water taken up by most rubber compounds is taken up by the soluble impurities in the compounds. The amount of water taken up by these soluble constituents should not be dependent upon the combined sulphur content except as it is affected by the rigidity which the sulphur imparts to the rubber, assuming that the sulphur does not react with the soluble constituents.

In Table VI are tabulated the water contents of sheets of various combined sulphur contents after 7 days and after 210 days immersion in sodium chloride solution of various vapor pressures. The results are shown graphically in Figs. 9 and 10. The amount of water absorbed by the compounds as the combined sulphur content increases does not decrease continuously as might be expected but a break in the curve is apparent at a sulphur content of about 7% even after a period of only 7 days immersion. The break becomes a peak in the curve after longer periods of immersion. It is believed that this peak is caused partly by a slow oxidation of the sheets even when

immersed in solution. Certain other data indicate that the rate of oxidation of straight rubber sulphur compounds is greatest for a combined sulphur content of about 7% and it will be shown later that oxidized rubber absorbs more water than does unoxidized rubber. In the case of sheets sealed up in glass tubes free from air the peak is much less pronounced. The nature of the compound itself is probably also related to the peak in the curve. In many ways rubber of from 6 to 10% combined sulphur differs markedly from either hard or soft rubber.

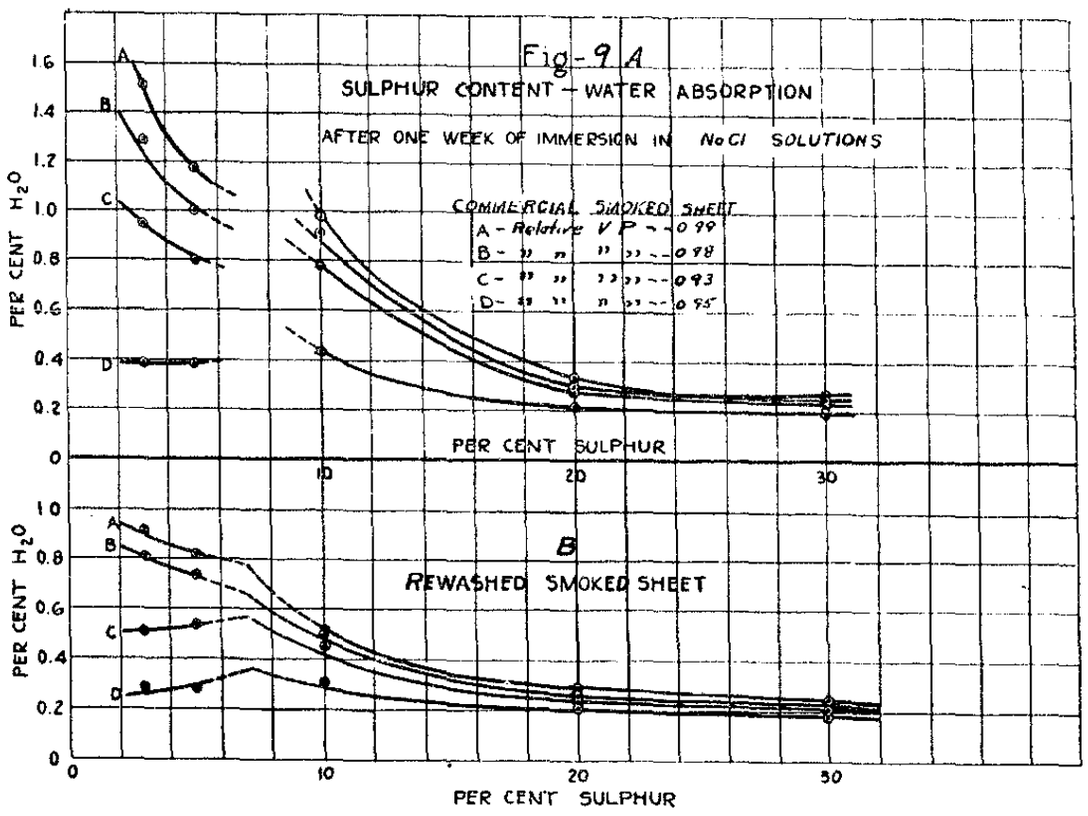


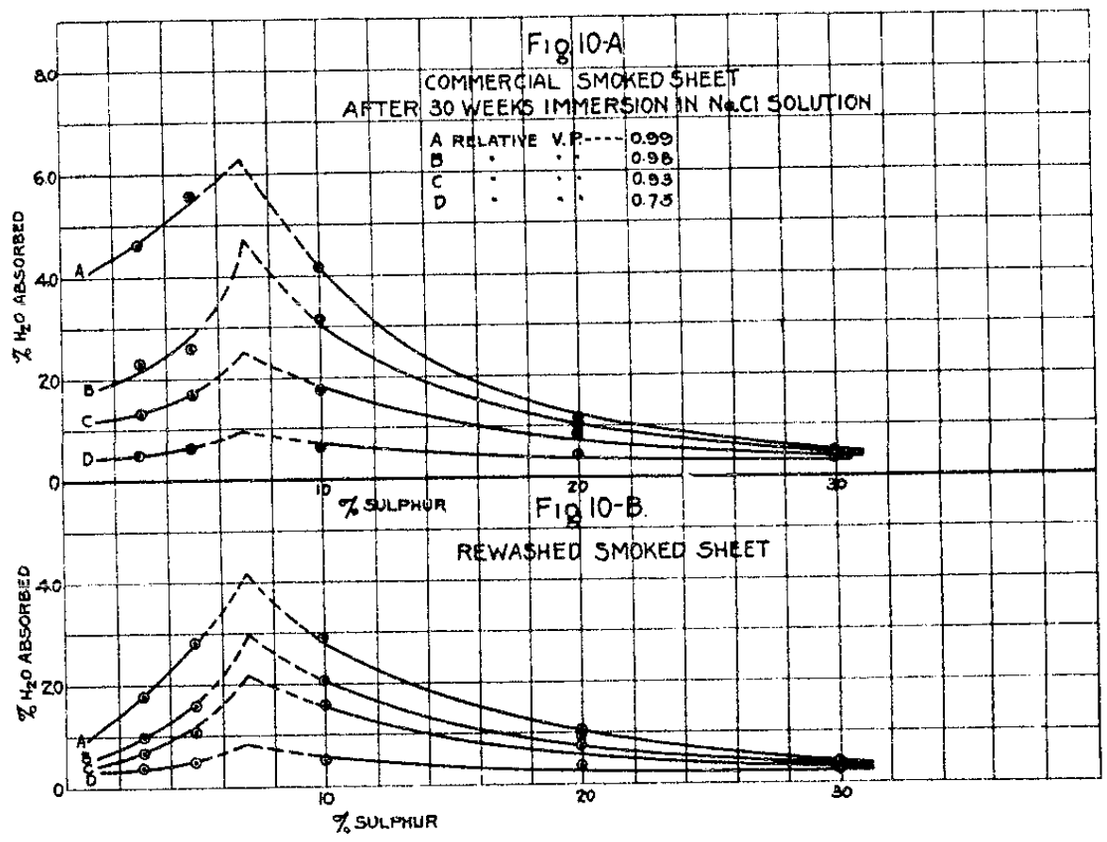
TABLE VI

Relation between Combined Sulphur Content and Water Absorption

Rewashed Smoked Sheet

%S.	Percent Water Absorbed After 7 and 210 Days Immersion							
	P/P_o = .995		P/P_o = .978		P/P_o = .930		P/P_o = .750	
	7	210	7	210	7	210	7	210
3	0.91	1.74	0.81	0.93	0.51	0.64	0.29	0.33
5	0.82	2.80	0.74	1.58	0.54	1.09	0.28	0.45
10	0.51	2.86	0.50	2.08	0.45	1.57	0.31	0.48
20	0.29	1.04	0.27	0.95	0.24	0.74	0.21	0.34
30	0.23	0.37	0.22	0.35	0.22	0.35	0.19	0.25
	Commercial Smoked Sheet							
3	1.52	4.61	1.29	2.26	0.95	1.25	0.39	0.48
5	1.18	5.53	1.01	2.56	0.80	1.67	0.38	0.59
10	0.99	4.17	0.92	3.13	0.78	1.75	0.44	0.61
20	0.34	1.15	0.31	1.09	0.30	0.82	0.22	0.41
30	0.29	0.47	0.27	0.45	0.23	0.43	0.21	0.31

In spite of this break in the curves the effect of rigidity can be observed in those shown in the Figs. 9 and 10. There is a very great difference in the amount of water absorbed by the rewashed and commercial rubber in the case of rubber having a low combined sulphur content which is very soft. As the sulphur content is increased and the rubber becomes more rigid this difference disappears. The amount of water absorbed by both rewashed and commercial rubber depends to a very great extent upon the vapor pressure of the solution when the sulphur content is low and the rubber is soft and elastic.



When the sulphur content is high and the rubber is very rigid this effect of vapor pressure is very greatly diminished. It will be noted that the amount of water absorbed by the most rigid sheets (highest sulphur content) is even less than that held in true solution by raw rubber or rubber of low combined sulphur content.

The Effect of Temperature upon Water Absorption

The proposed theory would predict that the higher the temperature the greater the rate of absorption of water by a rubber compound since greater differences in vapor pressure of water external and internal differences in vapor pressure of water external and internal to the rubber sheet are possible at higher temperatures and these differences are the driving forces causing water to enter the sheet. Also, rates of diffusion will be higher, the higher the temperature. The theory would also predict that the amount absorbed at equilibrium should not be greatly affected by temperature because the temperature coefficient of vapor pressure is not greatly different for different

solutions and also relative vapor pressure is very nearly independent of temperature, as is shown by the figures of Table VII. If the rigidity of the compounds is appreciably decreased by increasing temperature the amount of water absorbed would be increased. This has been observed for certain thermoplastic compounds and for vulcanized rubber at high temperatures (40-70°C.).

TABLE VII

Change in the Relative Vapor Pressure of a 4.75% Sodium Chloride Solution with Temperature

Temp. (°C)	P_o	P	P/P_o
20	17.53	17.0	0.970
30	31.82	30.8	0.968
40	55.32	53.6	0.969
50	92.51	89.7	0.970
60	149.4	144.9	0.970
70	233.7	226.6	0.970
80	355.1	344.3	0.970
90	525.8	509.9	0.970

P_o = Vapor Pressure of Pure Water
P = Vapor Pressure of Solution

The data of Table VII were taken from Landolt-Börnstein: Physikalisch-Chemische Tabellen.

If a sheet of rubber had reached equilibrium at one temperature, a change in temperature would result in a change of vapor pressure of both the solution internal to the rubber sheet and of that external to the sheet. If this change in each case were the same, equilibrium would not be disturbed.

In order to test these conclusions experimentally both the rate of absorption and the equilibrium amounts absorbed by several different rubber compounds were determined at 0°, 15°, 25°, and 40°C. The equilibrium amounts

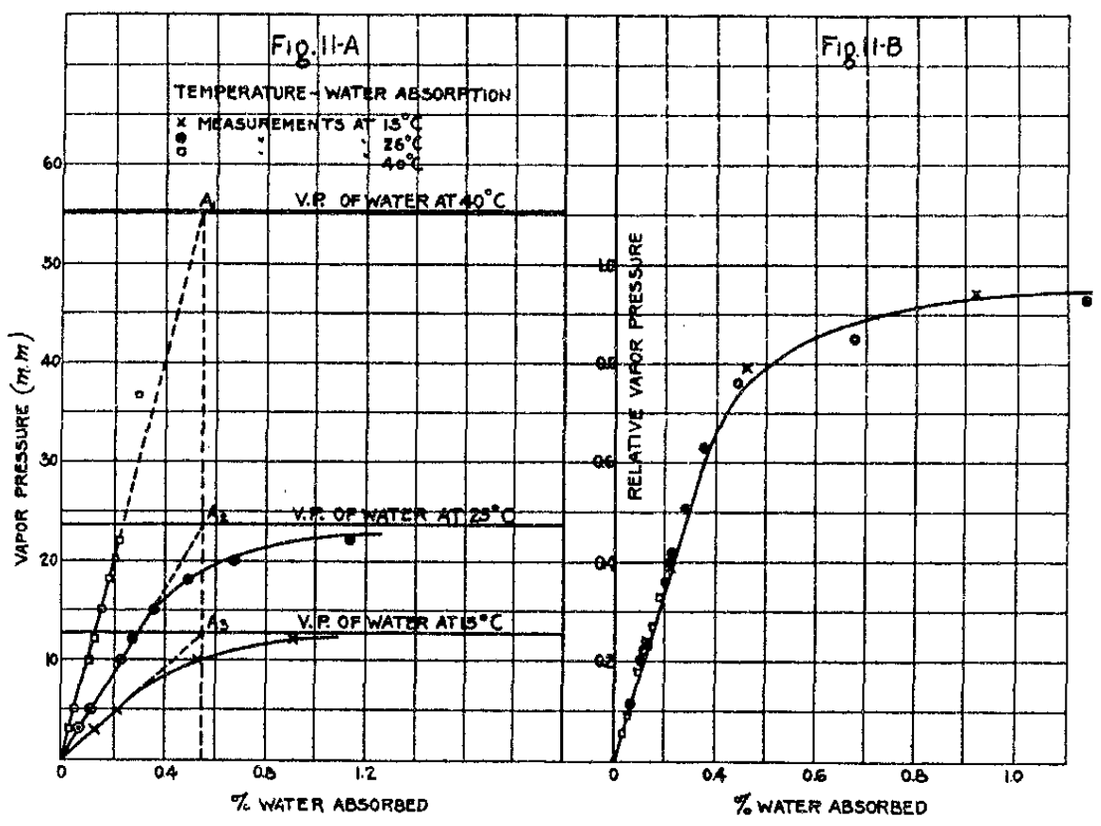
TABLE VIII

Temperature—Water Absorption

P(m.m.)	P/P		% Water Absorbed by Compounds A, B, and C					
	25°	40°	25°	40°	25°	40°	25°	40°
3.0	0.13	0.055	0.03	0.013	0.06	0.035	0.15	0.070
5.0	0.21	0.091	0.04	0.020	0.10	0.052	0.23	0.110
10.0	0.42	0.18	0.09	0.043	0.21	0.100	0.47	0.207
15.0	0.63	0.27	0.14	0.065	0.31	0.142	0.68	0.310
18.0	0.76	0.33	0.16	0.079	0.38	0.175	0.88	0.371
20.0	0.85	0.36	0.21	0.087	0.50	0.190	1.21	0.410
22.0	0.93	0.40	0.30	0.095	0.80	0.210	1.53	0.450
23.0	0.975	0.418	0.41	0.100	1.30	0.220	2.05	0.470
23.2	0.983	0.423	0.52	0.101		0.221		0.472

Compound A, Filled (Silica) Compound
B, Gutta Percha Cable Compound
C, Gutta Percha

absorbed at various vapor pressures were first studied by Method (2), the temperature of the thermostat in which the bulbs containing the samples were immersed being regulated to the various temperatures. It is evident that the experiments could not be carried out at pressures of water vapor above that of water at the lowest temperature of the laboratory, which was about 25°C, because condensation of moisture would take place in the apparatus and prevent the pressure being raised above this limit. For this reason the complete vapor pressure curve could not be determined at 40°C.



The results of these experiments are presented in Tables VIII and IX, and those for one compound are shown graphically in Fig. 11. From these it is seen that for a given vapor pressure the amount of water absorbed increases with decreasing temperature, but this does not mean that a sheet of rubber immersed in a salt solution or sea water will absorb less the higher the temperature, as will be evident after studying the figures. It will be noted that if the straight portions of the curves be extended to the line representing the vapor pressure of pure water the intersection for a given sample at the respective temperatures, for example A_1, A_2 and A_3 of Fig. 11A, all lie at the same water content. This means that if relative vapor pressures were plotted instead of absolute vapor pressures the curves for the different temperatures for a single compound would all coincide. The curves of Fig. 11A are plotted in this way in Fig. 11B. As relative vapor pressure is practically independent of temperature, as is shown by Table VII, Fig. 11B should be a single curve within certain limits. These limits are determined by the similarity of the

TABLE IX

Absorption of Water by Commercial Smoked Sheet (3% Combined Sulphur) at 15, 25, and 40°C.

P(m.m.)	P/P$_o$			% Water Absorbed at Equilibrium		
	15°	25°	40°	15°	25°	40°
3	0.24	0.13	0.055	0.13	0.07	0.03
5	0.39	0.21	0.091	0.22	0.11	0.05
10	0.79	0.42	0.18	0.53	0.23	0.10
12	0.94	0.51	0.22	0.92	0.28	0.12
15	——	0.63	0.27	——	0.36	0.15
18	——	0.76	0.33	——	0.50	0.18
20	——	0.85	0.36	——	0.68	0.20
22	——	0.93	0.40	——	1.15	0.22

soluble impurities in rubber to sodium chloride in respect to changes of the relative vapor pressure of their solutions with temperature, and also to change of solubility with temperature.

In order to study the effect of temperature upon the rate of absorption Method (1) was used. The humidifiers were placed in a constant temperature room, the temperature of which was regulated to 0°C+1°. Method (3) was used to determine equilibrium amounts at 0°. The results of these experiments are presented in Tables X-XIV and representative values plotted in Fig. 12. These results show plainly that the rate of water absorption is higher, the higher the temperature but they also show, that the amount absorbed at equilibrium is not greatly affected. The water content of the

TABLE X

50 mil Sheets immersed in 3.5% NaCl Solution at 0°C. Rewashed Smoked Sheet

% Sulphur Content		% water absorbed after specified time intervals (days)			
Total	Free	5	16	34	71
3	0.58	0.33	0.47	0.62	0.66
5	1.12	0.27	0.41	0.57	0.57
10	0.30	0.21	0.36	0.59	0.73
15	0.82	0.17	0.24	0.30	0.41
20	0.13	0.07	0.13	0.18	0.21
30	0.51	0.06	0.12	0.15	0.18
		Commercial Smoked Sheet			
3	0.17	0.64	1.02	1.42	1.84
5	0.16	0.52	0.83	1.14	1.47
10	0.15	0.36	0.58	0.81	1.18
20	0.14	0.10	0.18	0.23	0.30
30	0.50	0.12	0.18	0.21	0.26
Filled (Si.) Comp.		0.23	0.30	0.37	0.44
Filled (H. R. D.) Comp.		0.29	0.39	0.49	0.60

All values given are averages of two values for duplicate sheets.

commercial rubber sheets at 0° at the end of 71 days is still much below that at 25°, but experience has shown that commercial rubbers do not reach equilibrium nearly as rapidly as do rewashed rubbers.

TABLE XI

50 mil Sheets Immersed in 18.4% NaCl Solution at 0°C.

Rewashed Smoked Sheet

% Sulphur Content		% water absorbed after specified time intervals (days)			
Total	Free	5	16	34	71
3	0.58	0.30	0.38	0.40	0.37
5	0.12	0.23	0.29	0.34	0.31
10	0.30	0.19	0.28	0.40	0.49
15	0.82	0.11	0.18	0.25	0.30
20	0.13	0.07	0.13	0.16	0.16
30	0.51	0.06	0.12	0.14	0.14
		Commercial Smoked Sheet			
3	0.17	0.44	0.62	0.75	0.71
5	0.16	0.33	0.54	0.65	0.66
10	0.15	0.27	0.41	0.58	0.72
20	0.14	0.07	0.15	0.20	0.23
30	0.50	0.06	0.13	0.18	0.21
Filled (Si.) Comp.		0.14	0.20	0.24	0.24
Filled (H. R. D.) Comp.		0.20	0.26	0.31	0.32

All values given are averages of two values for duplicate sheets.

TABLE XII

50 mil Sheets immersed in Saturated NaCl Solution at 0°C.

Rewashed Smoked Sheet

% Sulphur Content		% Water absorbed after specified time intervals (days)			
Total	Free	5	16	34	71
3	0.58	0.22	0.26	0.25	0.26
5	1.12	0.14	0.18	0.19	0.20
10	0.30	0.17	0.22	0.28	0.34
15	0.82	0.15	0.18	0.20	0.24
20	0.13	0.07	0.11	0.13	0.15
30	0.51	0.06	0.09	0.12	0.13
		Commercial Smoked Sheet			
3	0.17	0.32	0.41	0.43	0.45
5	0.16	0.28	0.36	0.41	0.41
10	0.15	0.27	0.35	0.43	0.51
20	0.14	0.10	0.14	0.17	0.20
30	0.50	0.09	0.13	0.16	0.17
Filled (Si.) Comp.		0.09	0.13	0.12	0.13
Filled (H. R. D.) Comp.		0.13	0.17	0.18	0.19

All values given are averages of two values for duplicate sheets.

TABLE XIII

50 mil Sheets immersed in 3.5% NaCl Solution at Room Temperature.
Rewashed Smoked Sheet

% Sulphur Content		% water absorbed after specified time intervals (days)			
Total	Free	5	16	34	71
3	0.58	0.63	0.69	0.70	0.68
5	1.12	0.51	0.59	0.58	0.59
10	0.30	0.57	0.80	0.93	1.22
15	0.82	0.43	0.64	0.71	0.87
20	0.13	0.22	0.36	0.38	0.44
30	0.51	0.20	0.23	0.23	0.24
Commercial Smoked Sheet					
3	0.17	1.74	2.51	2.84	3.13
5	0.16	1.36	2.05	2.34	2.58
10	0.15	1.20	1.83	2.14	2.54
20	0.14	0.36	0.63	0.74	0.88
30	0.50	0.25	0.35	0.34	0.37
Filled (Si.) Comp.		0.38	0.40	0.43	0.46
Filled (H. R. D.) Comp.		0.53	0.58	0.60	0.66

All values given are averages of two values for duplicate sheets.

TABLE XIV

Equilibrium Values at 0°C.
Rewashed Smoked Sheet

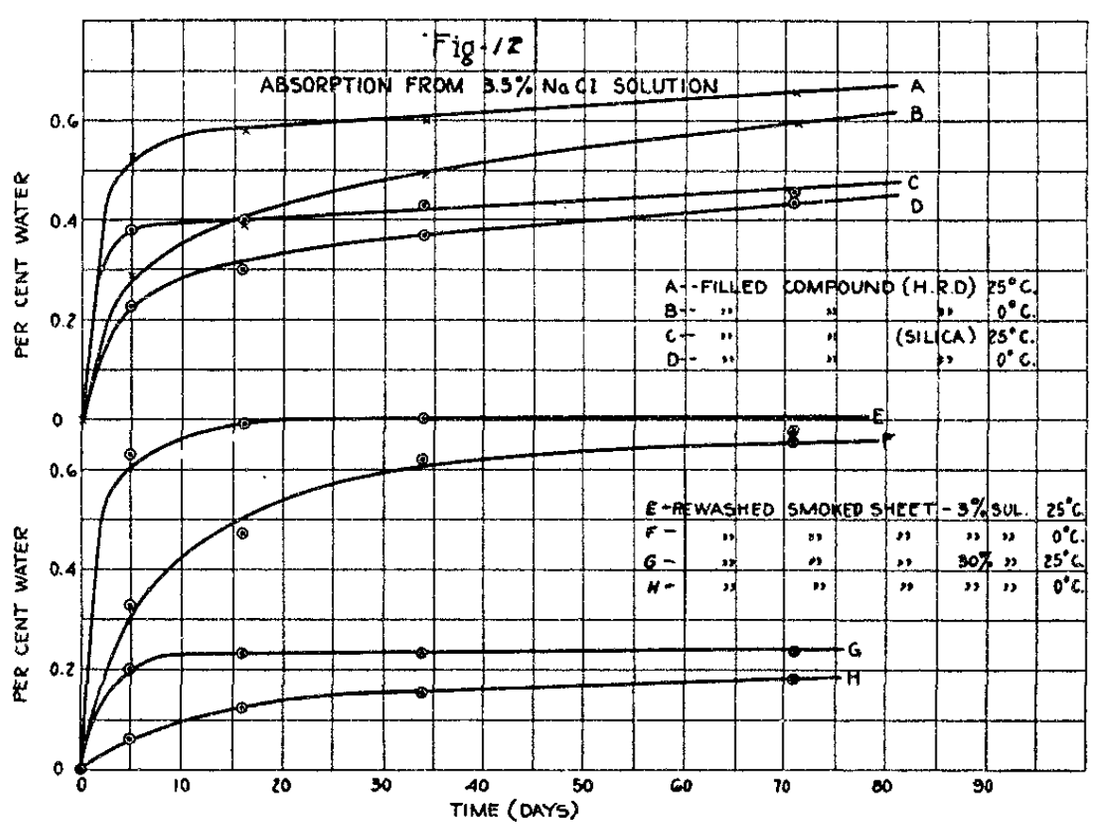
% Sulphur Content		% water absorbed at equilibrium		
Total	Free	3.5% NaCl Sol	18.4% NaCl Sol	Sat. NaCl Sol
3	0.58	1.14	0.51	0.31
5	1.12	1.01	0.47	0.28
10	0.30	1.90	1.00	0.71
15	0.82	1.24	0.70	0.57
20	0.13	0.75	0.42	0.26
30	0.51	0.53	0.30	0.19
Commercial Smoked Sheet				
3	0.17	3.84	0.92	0.50
5	0.16	3.18	0.82	0.55
10	0.15	2.64	0.91	0.69
20	0.14	1.62	0.56	0.31
30	0.50	0.75	0.30	0.22
Filled (Silica Comp.)		0.61	0.28	0.19
Filled (H. R. D.) Comp.		0.96	0.50	0.31

All values given are averages of two values for duplicate samples.

The equlibrium values given in Table XIV show that all of the samples at 0°C. have absorbed more water than the corresponding 50 mil sheets at 25° after a period of 71 days. The results are also in fair agreement with those of

similar sheets immersed at room temperature for a period of 200 days. At the lower vapor pressures (saturated salt solution) where most of the impurities do not have a part in water absorption the agreement is probably within the experimental error. (see Table 1E)

The results of these experiments explain the apparently contradictory results obtained by Miss van de Leur[1] who observed that the amount of water absorbed by rubber compounds from pure water greatly increased with temperature but did not seem to be influenced appreciably at lower relative



vapor pressures. According to the proposed theory the rate of absorption of water increases with temperature, and also compounds immersed in distilled water should continue to absorb water indefinitely. Therefore when sheets of rubber are immersed in distilled water or suspended in the vapor above distilled water the amount of water absorbed after definite time intervals will be greater the higher the temperature. The theory demands and experimental results show that from solutions of P/P_o below 1, compounds absorb a definite amount of water corresponding to the value of P/P_o, and that the amount is not greatly dependent upon temperature. Therefore the only effect of an increase in temperature at relative vapor pressures below unity should be an increased rate of approach to equilibrium. In the case of rubber containing a relatively high percentage of water soluble material temperature probably does have a slight effect upon the equilibrium amount of water absorbed as is shown by Figure 12. More water is absorbed at the higher temperature.

[1]Kolloidchem. Beihefte **10**, 45 (1918).

This is probably caused by a difference in the temperature coefficients of vapor pressure of solutions of the impurities in the rubber and of the solution in which the rubber sheets are immersed.

The "puzzling" results obtained by Obach[1] and commented upon by Kirchoff,[2] showing that although the temperature of sea water fluctuated

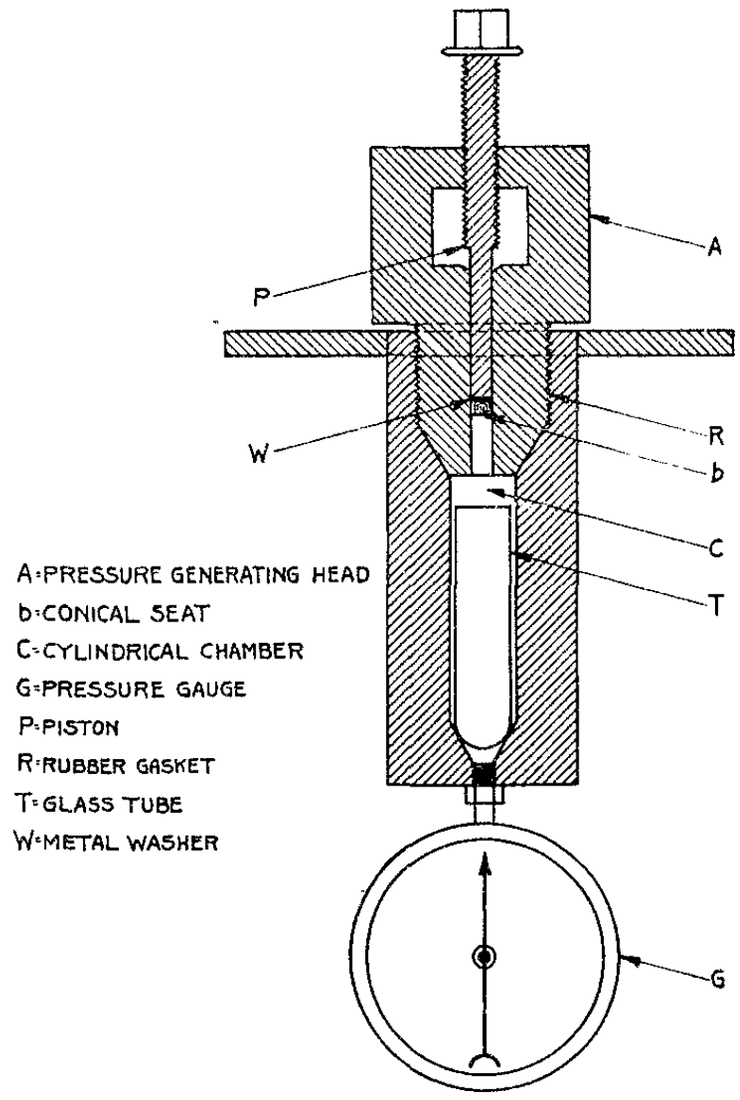


FIG. 13

between 14° and 25°C., the water content of raw rubber immersed in it remained constant after the first two weeks immersion, also are in accord with the theory and the above experimental results.

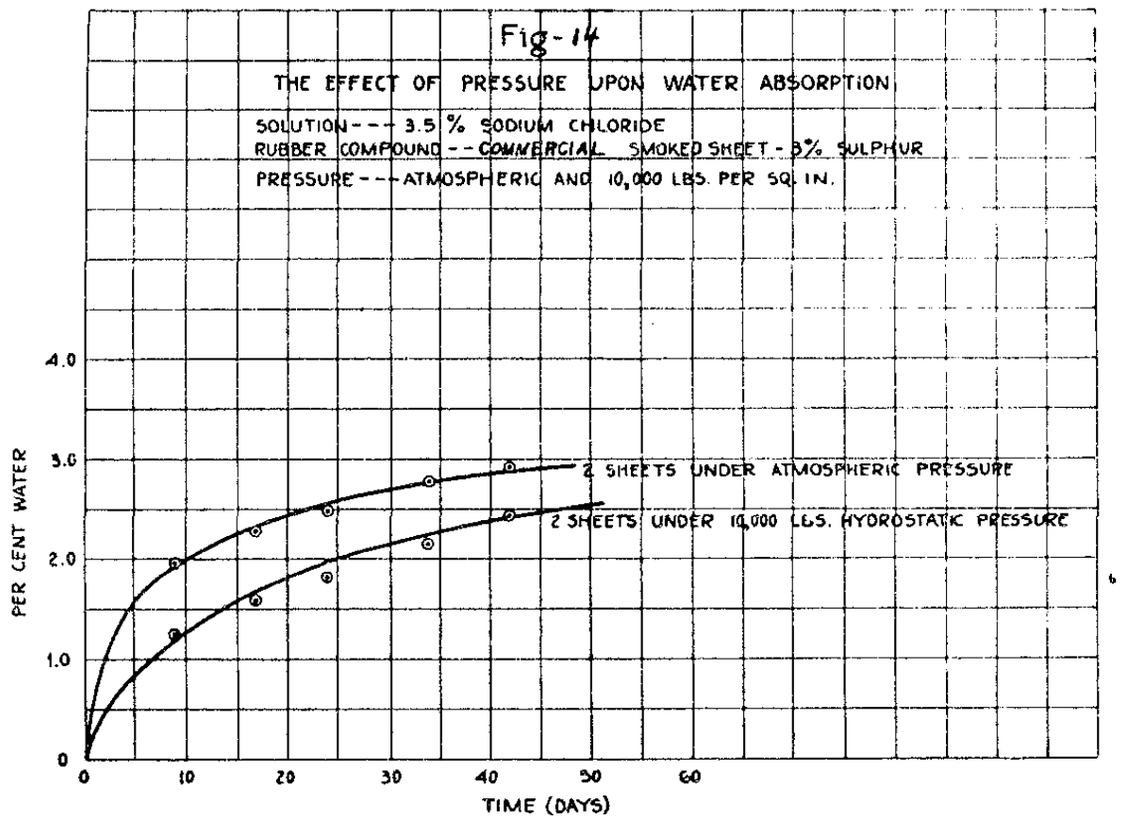
The Effect of Hydrostatic Pressure Upon Water Absorption.

Rubber compounds used for submarine insulating purposes are often subjected to considerable hydrostatic pressure. It is of interest therefore, not only from the theoretical but also from the practical standpoint, to know how hydrostatic pressure affects water absorption. To determine this experimentally the pressure bomb illustrated in Fig. 13 was constructed. Sheets of

[1] "Cantor Lectures on Gutta Percha," Appendix VIII, p. 100 (1898).

[2] Kolloid-Z., 35, 367 (1924).

various rubber compounds were placed in a 3½% salt solution in the Tube T, the chamber filled with oil and pressure applied by screwing down the piston P. The pressure used in the experiment was 10,000 lbs. per sq. in. which is equivalent to approximately four miles of hydrostatic pressure. The absorption of water at atmospheric pressure was alwaysy determined along with the determinations at high pressure for comparison purposes.



The experimental data are given in Tables XV and XVI and those of Table XVI are plotted in Fig. 14. The results given in the column headed "Differences" are the differences of the average water content of the sheets at atmospheric pressure and 10,000 lbs. pressure. The figures show, as do the curves, that these differences become smaller with time, indicating that the rate of water absorption is slower under the high pressure. The reason for this is probably the effect of pressure upon the density of the rubber compound, causing the rate of diffusion of water in the sheet under pressure to be slower. If this explanation is the correct one, a soft rubber compound would be expected to be affected to a greater extent by hydrostatic pressure than more rigid ones. The results given in Tables XV and XVI show that this is the case. The filled rubber compound is much more rigid than the rubber-sulphur sheet and the values given in the "Difference" column are much larger for the latter than for the former compound.

In order to determine the effect of pressure upon the equilibrium amount of water absorbed several sheets of rubber which had apparently very nearly reached equilibrium at atmospheric pressure were subjected to the high pressure and the change in water content observed. The results are tabulated

in Table XVII and XVIII. They indicate that the effect on the equilibrium amount of water absorbed, if any, will be very small. Those under pressure appear to absorb very slightly the greater amount of water.

TABLE XV

The Effect of Hydrostatic Pressure on Water Absorption
Filled (Silica) Compound

Elapsed Time (Days)	% gain in weight Atm. P. Sheet 1,	Atm. P. Sheet 2	10,000 lbs. P. Sheet 1,	10,000 lbs. P. Sheet 2	Averages Atm. P.	Averages 10,000 lbs. P.	Diff.
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5	0.30	0.31	0.18	0.21	0.305	0.195	0.110
9	0.34	0.33	0.25	0.27	0.335	0.260	0.075
Sheets Replaced by New Ones							
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
14	0.46	0.46	0.40	0.40	0.46	0.40	0.06

TABLE XVI

The Effect of Hydrostatic Pressure on Water Absorption
Commercial Smoked Sheet, 3% S.

Elapsed Time (Days)	% gain in weight Atm. P. Sheet 1,	Atm. P. Sheet 2	10,000 lbs. P. Sheet 1,	10,000 lbs. P. Sheet 2	Averages Atm. P	Averages 10,000 lbs. P	Diff.
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
9	1.89	2.02	1.26	1.24	1.96	1.25	0.71
17	2.20	2.33	1.62	1.54	2.27	1.58	0.69
24	2.41	2.55	1.87	1.76	2.48	1.81	0.67
37	2.71	2.85	2.22	2.08	2.78	2.15	0.63
42	2.84	3.03	2.45		2.93	2.45	0.48

TABLE XVII

The Effect of Hydrostatic Pressure on the Equilibrium Amount of Water absorbed by Filled Rubber

Sheet No.	% H_2O at Saturation	Wt. at Saturation	Wt. after 24 hrs. under 10,000 lbs. P.	% Wt. gain
I	0.49	4.0860	4.0857	−0.007
II	0.49	4.2428	4.2437	+0.021

Sheets I and II were Filled (Silica) Compound.

TABLE XVIII

The Effect of Hydrostatic Pressure on the Equilibrium Amount of Water absorbed by Unfilled Rubber

Sheet No.	% H_2O at Saturation	Wt. Saturation	Wt. after 1 Month Atm. P.	Wt. after 1 Month 10,000 lbs. P.	% Wt. Gain
I	3.22	2.0723	2.0738	——	0.072
II	3.18	1.9204	1.9222	——	0.093
III	3.18	1.8694	——	1.8715	0.112
IV	3.14	1.8031	——	1.8049	0.100

The sheets used in the above experiment had the following composition:

Commercial Smoked Sheet	95.0%
Combined Sulphur	4.25%
Free Sulphur	0.75%

The results of the experiments under high hydrostatic pressure are again in harmony with the theory. They are not in agreement however with those of E. Schulze[1] who found that pressures of 150 lbs. per sq. in. increased the amount of water absorbed very greatly. Pressure applied to water or to a solution in such a way that the vapor is free to escape increases the vapor pressure of the water or solution. This increase in the case of water is about one part in one thousand for an increase of pressure of one atmosphere. It is given by the equation $dp/Pd = v/V$ in which p is the vapor pressure of the water, P the externally applied pressure, v the molecular volume of the liquid, and V the molecular volume of the vapor. If the pressure upon the solution in which the rubber sheet is immersed is greater than that upon the solution internal to the rubber the amount of water absorbed should be theoretically increased. The above condition is probably true to a slight extent in the case of porous sheets which are very rigid because the rigidity of the compound would have a tendency to counteract some of the pressure which is exerted upon the external solution. It has been shown, however, by Le Roux[2] and Terry[3] and the writers have found that well-made rubber sheets are not porous.

The amount of water absorbed under pressure would also be increased by the pressure if the volume of the water absorbed by the rubber sheet plus the volume of the dry rubber were greater than the water-rubber solution after absorption. It has been shown by M. Payen[4] and by Le Roux[5] that rubber sheets expand in volume to an extent very nearly equal to or probably slightly less than the volume of water absorbed. The writers have also found that the weight of sheets of rubber immersed in a solution and weighed while immersed gain only very slightly in weight which is further evidence that rubber expands in volume very nearly equal to the volume of water absorbed.

The Influence of Aging upon Water Absorption

It will be noted that in certain cases rubber compounds apparently do not reach an equilibrium when immersed in a salt solution. As has already been stated, this might be caused by a change taking place in the sheet with time. In order to determine this and also to determine the effect of aging which is generally agreed to be oxidation, upon the absorption of water by rubber compounds experiments of the following nature were performed:

1. Sheets of a rubber compound were sealed in tubes filled with a salt solution and sheets of the same compound also immersed in solutions in contact with air.

2. Sheets of rubber compound were aged artificially by passing oxygen over the heated sheets and also by heating in an aging oven in air.

3. Sheets of a compound which had previously been studied as regards absorption of water and other properties and which appeared to have aged

[1] Gummi Ztg., **12**, 118 (1898).
[2] Compt. rend., **63**, 917 (1866).
[3] India Rubber World, **23**, 107 (1901).
[4] J. Prakt. Chemie **55**, 109 (1853).
[5] Compt. Rend. **63**, 917 (1866).

were redried and again studied in the same manner to determine the effect of any change that had taken place in the sheets.

The results given in Table XIX show the effects of air upon sheets immersed in 3.5% salt solution. The sheets of series A were sealed up in glass tubes filled with the solution which had been pumped free of air before sealing. The sheets of series B were immersed in the same solution contained in wide-mouthed bottles and closed with rubber stoppers. Those of series C were immersed in an open beaker filled with this solution and placed in a large, covered desiccator. It is apparent from the results tabulated in the tables that those sheets with which air could most easily come in contact gain the most in weight.

In order to determine whether or not the peak in the curves representing the amount of water absorbed with variation in sulphur content (Figs. 9 and 10) might be due to an oxidation of the rubber sheets under water which takes place at the greatest rate in the case of rubber compounds of approximately 7% combined sulphur, sheets of rubber were immersed in a 3.5% sodium chloride solution and sealed up in evacuated tubes. Several tubes were prepared and after a tube had once been broken open and the sheets weighed, the sheets were discarded except in the case of the first tube. The sheets in this tube were immersed in a 3.5% sodium chloride solution exposed to the air and weighed periodically. The results of this experiment are shown in Table XX.

The results show that the peak does not appear in case of sheets sealed up in tubes free from air, but in the case of sheets which were not sealed up the amount of water absorbed after 233 days increases rapidly with combined sulphur content up to a sulphur content of 7%. The compounds used in this experiment were made to be as nearly like those used in the experiment shown graphically in Fig. 10B as possible and the experimental results are also in agreement.

TABLE XIX

The Influence of Exposure to Air on the Absorption of Water Rewashed Smoked Sheet, 5% Sulphur

	Series A	Series B	Series C
Sample No.	% Wt. Gain	% Wt. Gain	% Wt. Gain
1	0.72	0.89	0.92
2	0.77	0.82	0.96
3	——	0.85	1.05
4	0.72		
5	0.73		
6	0.67		
Averages—	0.72	0.85	0.98

The values given in Table XIX are the percent weight gains after a period of three months' immersion in 3.5% sodium chloride solution.

TABLE XX

The Influence of Exposure to Air on the Absorption of Water Sheets Sealed in Glass Tubes

Sulphur Content	Gain in Weight After 14 Days	106 Days	316 Days
3	0.90	1.02	0.85
5	0.82	0.96	0.77
7	0.82	0.96	0.66

Sheets immersed in solution exposed to air.

	233 Days	284 Days
3	1.25	1.38
5	1.44	1.76
7	2.50	3.92

All data are the average values of two determinations

TABLE XXI

The Effect of Artificial Aging on the Absorption of Water Aged and Unaged Filled (Silica) Compound

Time (days)	A	B	C	D
7	0.29	0.23	0.35	0.53
14	0.33	0.27	0.36	0.57
28	0.34	0.28	0.41	0.60
98	0.35	0.33	0.43	0.61

Description of Sheets

Sheets A—Unaged
Sheets B—Nitrogen passed over sheets
Sheets C—Oxygen passed over sheets
Sheets D—Aged two weeks at 72°C in Geer Oven.

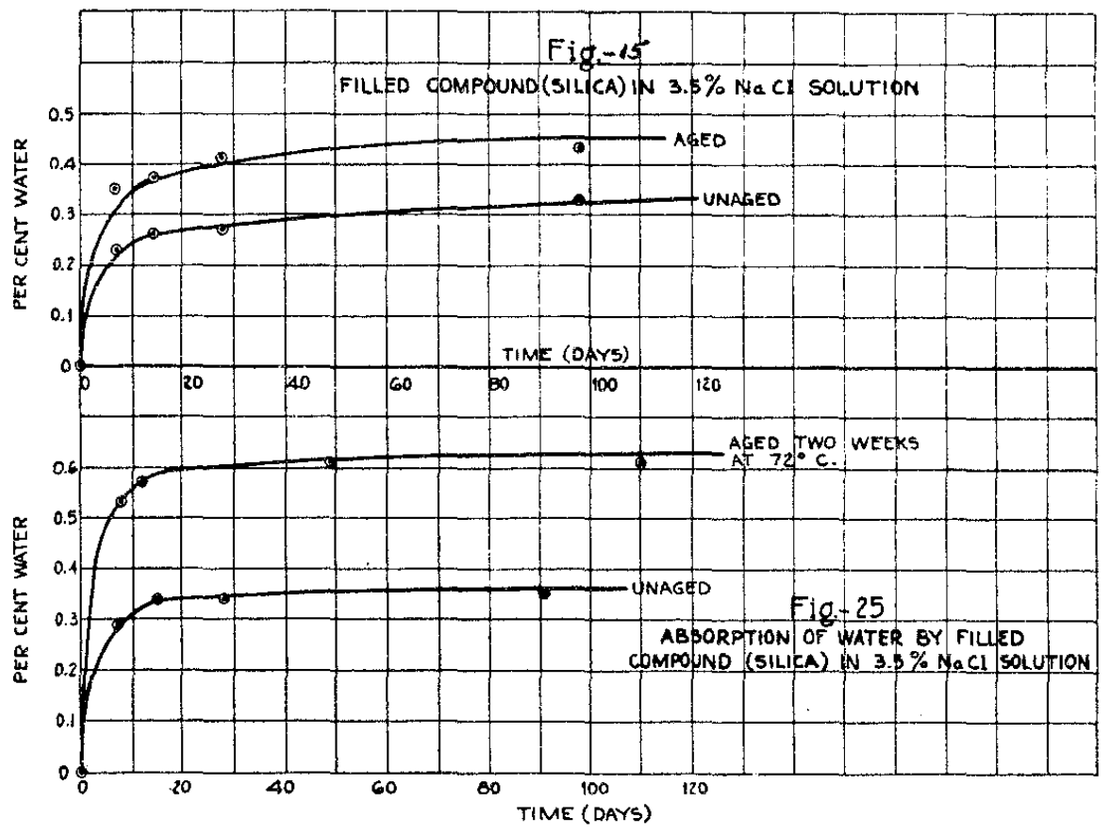
All values given are the average values of two determinations. The sheets were immersed in a 3.5% sodium chloride solution.

In Table XXI are tabulated data representing measurements made upon sheets of a filled cable compound which had been aged and also upon sheets of the same compound unaged. The aging in this case is artificial. The sheets were placed in an atmosphere of $P/P_0 = 0.98$ in a glass vessel so arranged that it could be heated to 100°C. The vessel was provided with an inlet at the bottom and an outlet at the top for the circulation of oxygen at atmospheric pressure. The sheets were heated in this manner for a period of three hours. For comparison purposes sheets were treated in a similar manner in an atmosphere of nitrogen. It is again apparent from the data of Table XXI plotted in Fig. 15 that the sheets aged in oxygen have taken up more water than those kept free from oxygen.

Sheets of the filled compound used in the previous aging tests were aged two weeks at 72°C. in an oven through which air was circulated (Geer test).

The results of tests made on the aged and unaged material are tabulated in Table XXI and plotted in Fig. 15. It is again apparent that the aging has resulted in an increase in the amount of water absorbed.

In order to determine to what extent aging of rubber compounds which have been kept under water effect the absorption of water, a few representative sheets which apparently had aged as determined by the character of the water absorption curve were redried and reimmersed and the course of the water absorption curve again determined. The data obtained during the first



and second periods of immersion of sheets of a compound composed of rewashed smoked sheet and five percent sulphur are presented in Table XXII and shown graphically in Fig. 16. The course after redrying is very different from the original course as is shown by curves A and B in Fig. 16. If the time origin of curve B is shifted to its proper position relative to the original curve A as shown by curve C it is seen that after a period of ten weeks curve C coincides with the original course of the curve extended.

These results indicate that the rubber compound has aged on the surface during immersion and after the aged sheet has been dried the aged material on the surface and the unaged material absorb water rapidly until saturation has been reached. The water content at this point corresponds to the water content at the end of the first period of immersion plus an additional amount due to additional aging of the sheet. After the aged sheet has become practically saturated the rate of water absorption is again controlled by the rate of

penetration of the film of aged material which determines the slope of the curve. It is possible that the slope of the curve may be of value in studying the aging of rubber compounds.

A surface film of aged material was very noticeable on sheets of the compound used in these experiments. Figure 17 is a photomicrograph of a cross-section of a sheet of the compound after a period of 520 days of immersion showing the film of aged material. The film appears white, probably because it contains a high percentage of water. While all the rubber compounds

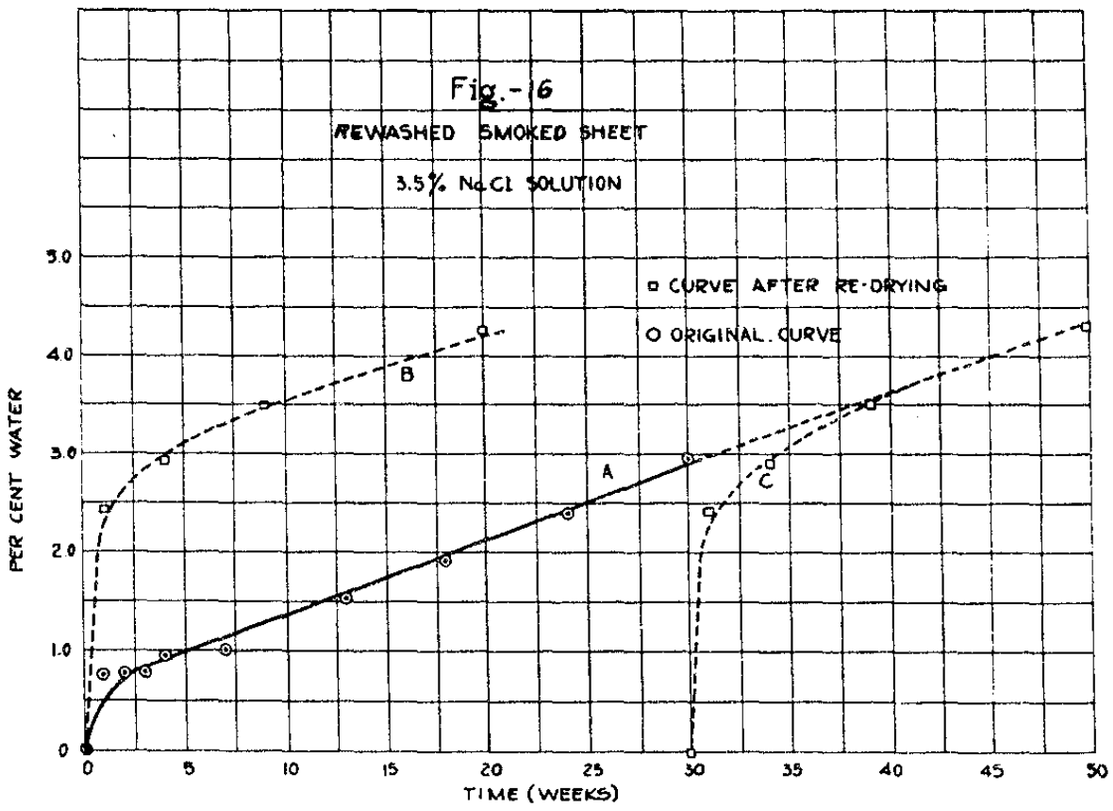


TABLE XXII

The Effect of Natural Aging under Water on the Absorption of Water

Time (days)	% Water absorbed from 3.5% Sodium Choride Sollution	
	Original Absorption	Absorption after Redrying
7	0.77	2.44
14	0.78	——
21	0.79	——
28	0.97	2.93
49	1.08	3.28
91	1.54	3.75
112	1.79	——
140	——	4.31
126	1.94	——
168	2.41	——
210	2.98	——

Values given are average values of two determinations.

studied do not show this effect of aging to such a marked degree, it is believed that this type of aging takes place to some extent in all types of rubber compounds which are exposed to air. Sheets of the same compound immersed in saturated sodium chloride solutions showed only slight evidence of having aged. The explanation of this may be the difference in solubility of oxygen in pure water and in salt solutions.[1]

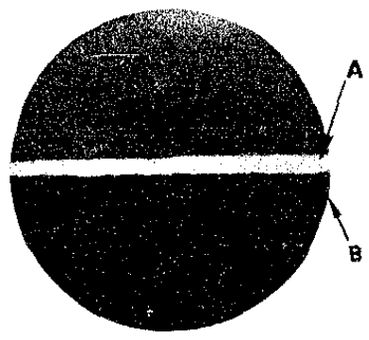


FIG. 17

Photomicrograph of a Cross-Section of an Aged Rubber Sheet.
Magnification—35 diameters.

A. Surface film of aged material on a rubber sheet after a period of 520 days immersion in a salt solution. The white appearance is probably due to a high concentration of absorbed water in the layer.

B. Interior of rubber sheet.

Summary and Conclusions

I. The complete vapor pressure curve for the system water-rubber has been determined for a number of rubber compounds.

II. The absorption of water from both the gaseous and the liquid phase has been studied and found to be the same in both cases provided the constituents other than water present in the phases do not enter the rubber or react with it.

III. It has been shown that washing rubber by a process which is described reduces the amount of water soluble constituents in the rubber and consequently the amount of water absorbed by rubber.

IV. The effect of combined sulphur content of rubber upon the amount of water absorbed has been investigated.

V. The rate of water absorption has been found to increase with temperature but in most cases the amount absorbed is not greatly dependent upon temperature.

VI. Hydrostatic pressure of 10,000 lbs. per sq. in. has been found to reduce the rate of water absorption but to have very little effect upon the amount absorbed at equilibrium.

VII. The amount of water absorbed by rubber compounds has been shown to be increased by a slow aging process which takes place even though the rubber compounds are immersed in solution if air is not excluded. This

[1] According to Fox, (Trans. Faraday Soc., **5**, 68 (1909)) the solubility of oxygen in distilled water at 25°C and atmospheric pressure is 0.02887 parts per part of water by volume reduced to N. T. and P. The solubility in a 12% sodium chloride solution under the same conditions, according to Geffcken (Z. physik. Chem., **49**, 257 (1904)) is .0145 parts per part of water.

aging takes place to the greatest extent on the surface. Rubber compounds of approximately 7% combined sulphur undergo this aging to the greatest extent.

The facts tabulated above have led to the following conclusions:

I. The most important factor determining the amount of water absorbed by a given sample of rubber is the vapor pressure of water with which it is in equilibrium.

II. The absorption of water by rubber appears to consist of two processes; the formation of a true solution of water in rubber, and the formation of solutions internal to the rubber of water soluble constituents of the rubber which can be removed by washing.

III. Increasing the rigidity of a rubber compound decreases greatly the amount of water absorbed.

Bell Telephone Laboratories, Inc.
New York, N. Y.

INVESTIGATION ON THE HEATS OF COMBUSTION OF PROPOSED SECONDARY STANDARD SUBSTANCES AND ON POSITION AND OPTICAL ISOMERS

BY LEON JEAN PIERRE KEFFLER AND FRANCIS CLINT GUTHRIE

The first aim of the present research has been to investigate the degree of precision that could be obtained for the water equivalent of an adiabatic calorimeter of special design, taking always the same initial and final temperatures for the calorimetric water, so as to make the readings relatively independent of the Beckmann thermometer used. Very concordant results were obtained with a sample of benzoic acid ("100%" pure) supplied by the Bureau of Standards.

The authors therefore considered that they were entitled to proceed.

1. To the determination of the heats of combustion of naphthalene and of salicylic acid and to add their contribution to that of P. Verkade and J. Coops[1] as to the desirability of the adoption by international agreement of a secondary standard for bomb calorimetry.

2. To the comparison of substances such as position and optical isomers whose heats of combustion are either equal to or only very slightly different from one another.

As the apparatus and method comprise several points, which are new the authors consider it of interest to describe them briefly.

Description of Apparatus and Method

The calorimeter is of the adiabatic submarine type, Fig. 1. It consists of two concentric silver-plated copper vessels, A and B, which are separated by an air gap *c* whose width was chosen as 16 mm. This is within the limits found by White[2] to correspond to optimum conditions for reducing to a minimum heat transference by conduction and convection. The inner vessel A—the calorimeter proper—weighs 623 grms. and is highly burnished on the outside. The outer vessel B is fitted with a flange at the top and covered with a copper lid D also highly polished on the silver plated lower surface. A water-tight joint was made by means of a rubber washer *w* and eight clamps disposed at equal intervals. The outer edges of the flange and lid were reinforced with stout copper bands E so as to prevent bending by the pressure of the clamps. The communication between the calorimeter proper and the outside was effected by means of four chimneys *a*, *b*, *c*, *d* soldered into the lid. To make the stirring as efficient as possible, the design proposed by Dickinson[3] for his non-adiabatic calorimeter was adopted. (see sketch). The whole was completely immersed (except for the four chimneys) in a large cylindrical copper

[1] Rec. Trav. chim., **43**, 567 (1924).
[2] J. Am. Chem. Soc., **40**, 379 (1918).
[3] Bur. Standards Bull., **6**, 189 (1914).

tank F full of water. Adiabatic conditions were obtained by electrolytic heating of this water, according to the method first suggested by Daniels.[1] As the current required was however beyond the limits of safety, the elasticity of the method was considerably increased by the use of a Dewar flask filled with nearly boiling water and communicating by means of rubber tubing with a circular lead pipe, pierced with holes and following the lower contour of the outer vessel. These holes were made of increasing diameter according to their distance from the feed pipe so as to ensure equal distribution throughout the tank. Stirring in the latter was effected by means of two propeller-type stirrers s and s' symmetrically disposed and driven by the same electric motor.

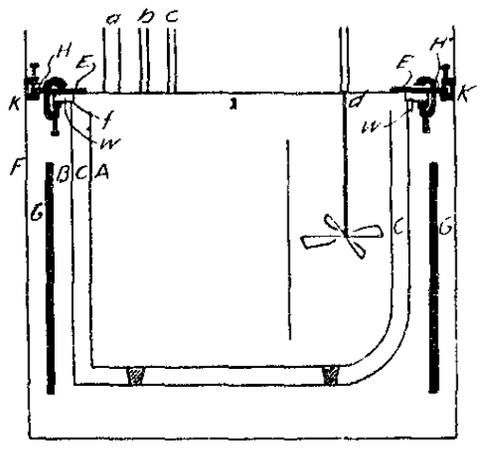
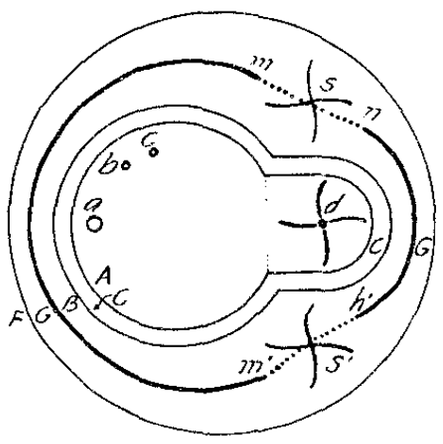



FIG. 1

The heating of the outer vessel, during the rapid rise in temperature which takes place at the beginning of the combustion, was controlled by allowing the hot water to flow in at a steady rate and making the fine adjustment of the temperature by varying the electric heating current. This variation was obtained by rising or lowering a copper sheet triangle in dilute sulphuric acid to the required depth. For maintaining the temperature of the outer jacket when it was several degrees above that of the air, a much smaller current was passed in series with a variable nichrome resistance.

Direct current only being available, neither of the thin copper jackets could be used as anode, as corrosion would have rapidly damaged them. A special anode was therefore constructed of thick copper sheet and shaped in the form of a belt equidistant from both jackets. It was supported on three stout ebonite forks, fitted inside small copper tubes, soldered to the bottom of the outer vessel. To make room for the stirrers, two windows mn and $m'n'$ were cut in the upper part of the anode.

The inside jacket was supported by means of two diametrically opposed projections H and H′ of the lid which fitted into two fork pieces, K and K′ soldered to the outer jacket. This ensured accurate centering and electrical connection between the two jackets which together constituted the cathode. This arrangement also increased safety in working the apparatus, even with the heavy currents employed, as the anode was well below the surface of the water.

[1] J. Am. Chem. Soc., **38**, 1473 (1916).

The bomb used was of the Berthelot-Mahler type, modified by Kroeker, and its capacity was 283 ccs. It was always evacuated for two minutes before being filled with oxygen, so as to reduce to a minimum the correction corresponding to the formation of nitric acid. The crucible was made of platinum and weighed 9.5 grms. Its dimensions were 25 mms. deep and 25 mms. diam. These were selected after experiments on various forms of crucibles, in view of the fact that no residue of carbon was left in the majority of cases investigated so far.

The comparison between the temperature of the calorimetric water and that of the outside vessel was effected by means of two thermometers graduated in tenths of a degree.

The rise of temperature inside the calorimeter was determined by means of a Beckmann thermometer graduated in hundredths of a degree, and standardised against the hydrogen scale by The National Physical Laboratory. The initial and final points on the scale were illuminated when required by two small electric lamps which, along with an electric hammer, were controlled by separate tapping key switches. Readings were made through a telescope to the nearest 0.0005°C, which corresponds to about two calories.

No Beckmann thermometer is so perfectly constructed as to allow of such a high degree of precision under the normal conditions of use. The concordance of the results first obtained was therefore notably improved by performing all the combustions under exactly the same initial and final conditions of temperature for the calorimeter and jacket. This was effected by weighing always the same amount of a given substance (within a few tenths of a milligram), so as to obtain exactly the same rise in each case.

Just before starting a combustion, the temperature of the calorimetric water was roughly adjusted to within a few tenths of a degree from the constant temperature selected as the starting point (15.38°C) and then brought to the exact value required by means of a specially constructed electric heater, thin enough to pass through one of the chimneys.

After the submarine system was immersed in the outer jacket the temperature of the latter was raised by "electrolytic" heating to the same point as that of the calorimeter. Soon after this equalisation was obtained, the first reading of the Beckmann was taken, then three more after intervals of five minutes. When the rise observed, due to the energy supplied by the stirrer to the calorimetric water, was found to be quite regular, the bomb was fired electrically by means of a platinum wire (.05 mm. diam.). This was wound round a cotton wick in contact with a pellet of the substance to be burnt. A constant weight, 6.3 to 6.5 grms was always taken, and gave thus a practically constant thermal effect, varying from 25 to 25.8 calories. Owing to the fineness of the platinum wire, the heat developed by the ignition current was found to be less than .2 calories and was therefore neglected.

The mercury column of the Beckmann was watched through the telescope so as to enable the supply of heat to the outer vessel to be started as soon as the mercury began to rise.

The uniform distribution of the heat of combustion was always complete after an interval of ten minutes, but the Beckmann was read at intervals of five minutes for a further quarter of an hour, so as to make sure that the rise in temperature per minute due to the friction of the stirrer was the same as that observed just before the ignition took place. This enabled an exact correction to be made for the heat of stirring. On the average this correction amounted to one hundredth of a degree (in ten minutes).

In accordance with the certificate supplied for the Beckmann thermometer by The National Physical Laboratory, a correction of three hundredths of a degree had to be added systematically to the constant range selected (1° to 4°C) in order to reduce it to the hydrogen scale. The water equivalent of the calorimeter was determined by burning six equal quantities of benzoic acid, supplied by the Bureau of Standards, Washington, and guaranteed 100% pure. The heat of combustion was given by the Bureau as 6329 cal. 20° in air (i. e. 6324 cal. 20° in vacuo). For the first two combustions the sample provided was used without drying and for the last four it was carefully dried by heating over an oil bath under reduced pressure.

One cc. of water was always put in the bomb before a combustion. Into the calorimeter were poured 3424 grms. of water (weight in vacuo) having a heat capacity of 3426.3 cal. 20°, at the mean temperature $\frac{1}{2}(15.37+18.38) = 16.88$°C at which all the combustions were carried out. The constancy of the temperature rendered no correction necessary for the variation of the heat capacity with temperature. The pressure used was always 25 atmospheres.

The heat capacity of the calorimeter proper and accessories was found to be equivalent to 325.1 ± 1.6 cal. 20° in vacuo, which gives for the total equivallent of the calorimetric system, the value 3751.4 ± 1.6 cal. 20° in vacuo. The results obtained are summarised in Table I.

The values which appear in the tenth column of that table, as well as in those summarising the experiments on heats of combustion, refer to the correction for unburnt carbon along with that due to carbon monoxide in the very few instances where the latter was found to be present. The determinations of carbon monoxide were made in a large number of cases arbitrarily chosen, but especially when traces of free carbon were apparent. The results obtained for the total correction due to incomplete combustion were small and less than the experimental error in general.

The actual estimation was carried out by passing the bomb gases through a train of potash wash-bottles, a soda-lime tube and a witness tube of baryta solution. The residual gases were then passed through a tube containing copper oxide, heated in an electric furnace and finally absorbed in a measured volume of standard baryta solution in such a manner that the gas stream was broken up into very small bubbles. The carbon monoxide content of the bomb gases was then obtained by titration of the baryta solution.

A test estimation was made on a known amount of carbon monoxide diluted with carbon dioxide and air to about the same extent as in the bomb gases. Analysis gave 11.7 ccs. of CO from 11.9 ccs. originally present.

TABLE I

Water Equivalent of the Calorimetric System

No. of Expt.	Corrected wt. of substance in air	Temp. observed in calorimeter initial	final	Correc. in thousandths stem	stirring	Corrected rise in °C	Correction in cal. for HNO_3	wool	C CO	Water Equivalent of bomb & calorimeter
1.	1.7900	0.9815	3.9850	2.5	6.3	3.0247	3.8	25.0	—	325.7
2.	1.7895	1.0035	4.0070	2.6	6.7	3.0242	2.1	25.8	2.0	324.2
3.	1.7893	0.9995	4.0025	2.3	7.0	3.0237	1.6	25.4	1.3	324.5
4.	1.7905	1.0020	4.0095	3.0	9.5	3.0250	3.7	25.8	—	326.7
5.	1.7894	1.0000	4.0050	1.7	9.2	3.0241	4.1	25.4	1.2	325.1
6.	1.7896	1.0005	4.0095	1.8	12.2	3.0250	4.5	25.0	0.8	324.5

General mean = 325.1 $cal_{20°}$. Maximum deviation from general = 1.6 $cal_{20°}$.

TABLE II

Heat of Combustion of Naphthalene

No. of Expt.	Corrected wt. of substance in air	Temp. observed in calorimeter initial	final	Correc. in thousandths stem	stirring	Corrected rise in °C	Correction in cal. for HNO_3	wool	Heat of combustion per gram.
1.	1.1598	0.9985	3.9550	1.5	5.0	2.9800	5.0	25.0	9613.1
2.	1.1772	1.0025	4.0050	2.5	5.5	3.0245	4.3	25.0	9613.4
3.	1.1771	1.0005	4.0050	2.5	6.5	3.0255	4.3	25.0	9615.8
4.	1.1771	0.9985	4.0025	2.0	6.5	3.0255	4.3	25.0	9615.8
5	1.1768	0.9930	3.9930	2.5	4.0	3.0235	2.0	25.4	9615.1
6.	1.1765	1.0025	4.0020	2.6	5.0	3.0219	2.3	25.4	9612.2

General mean = 9614.2 $cal_{20°}$ per gram weighed in air.
Maximum deviation from general mean = 2 calories.

Heat of Combustion of Naphthalene

One sample of pure naphthalene, supplied by the British Drug Houses (used for the two first combustions) and another one from Schuckaert (combustions 3 to 6) were both sublimed twice at the lowest possible temperature under reduced pressure. The results obtained are summarised in Table II.

This corresponds to the value *9606* cal. *20°* per gram in vacuo (at constant volume). These results agree well with those obtained recently by Dickinson, Richards and Davis,[1] Swientoslawski,[2] and Verkade,[3] as is shown clearly in Table III. In this table, for the sake of comparison the heats of combustion have been expressed in cal. 20° . The values obtained by the same observers for the ratio of the heat of combustion of naphthalene to that of benzoic acid are given in the fifth column.

TABLE III

Year	Observers	Heat of combustion per gram in air		Ratio
		Naphth.	Benzoic acid	
1914	Dickinson	9622	6329	1.5203
1917	Swientoslawski			
		9621	6316	1.5232
1920	Richards	——	——	1.5216
1924	Verkade	9623	6329	1.5204
1926	The authors	9614	6329	1.5190

Heat of Combustion of Salicylic Acid

The purest specimens obtainable from the British Drug Houses (see the first two combustions) and from Schuckaert (combustions 3 to 5) were both recrystallised three times from absolute alcohol, then from distilled water. After drying over calcium chloride and phosphoric anhydride in succession, they were recrystallised from heptane. The last traces of solvent were removed by heating in steam under reduced pressure. A third sample obtained from Poulenc Frères, and said to be the same as that used by Verkade and Coops[4] was first experimented upon without further purification (combustions 6 to 8). After crystallising from ether and freeing from any solvent by heating in vacuo, and finally drying by heating over phosphoric anhydride, a new group of combustions was obtained (combustions 9 to 11) The results are given in Table IV.

This corresponds to the value 5239 cal. 20° per gram in vacuo (at constant volume). These results are midway between those obtained recently, on the one side by Swientoslawski[5], Verkade[6], Roth[7] with a Beckmann thermometer, and on the other side by Berner[8] with a platinum resistance thermometer,

[1] J. Am. Chem. Soc., **42**, 1603 (1920).
[2] J. Am. Chem. Soc., **39**, 2595 (1917).
[3] J. Chem. Soc., **127**, 1437 (1925).
[4] Rec. Trav. chim., **43**, 567 (1924).
[5] Bull., **37**, 84 (1925).
[6] Rec. Trav. chim., **42**, 241 (1922); **43**, 567 (1924); J. Chem. Soc., **129**, 1437 (1926).
[7] Z. Elektrochemie, **30**, 607 (1924).
[8] J. Chem. Soc., **127**, 2747 (1925).

TABLE IV

No. of Expt.	Corrected wt. of substance *in air*	Temp. observed in calorimeter *initial*	*final*	Correc. in thousandths. *stem*	*stirring*	Corrected rise in °C	Correction in cal. for HNO_3	wool		Heat of combustion per gram
1.	2.1553	1.0070	4.0080	2.6	8.0	3.0204	2.1	25.8		5244.2
2.	2.1563	1.0075	4.0090	3.0	6.5	3.0220	3.4	25.4		5244.1
3.	2.1564	1.0085	4.0090	3.0	7.2	3.0203	2.4	25.0		5241.5
4.	2.1565	0.9935	3.9940	2.2	6.7	3.0216	2.4	25.4		5243.5
5.	2.1567	1.0010	4.0025	3.1	7.6	3.0208	2.6	25.4		5241.5
6.	2.1569	0.9805	3.9820	2.7	7.0	3.0218	2.4	25.8		5242.6
7.	2.1569	1.0060	4.0090	2.5	8.2	3.0223	2.4	25.4	C	5243.7
8.	2.1567	1.0025	4.0020	2.3	5.5	3.0217	2.2	25.4	+	5243.2
9.	2.1560	1.0060	4.0050	1.7	7.7	3.0196	2.4	25.4	CO	5241.9
10.	2.1568	0.9960	3.9985	1.5	9.0	3.0220	4.1	25.4	1.6	5242.9
11.	2.1568	1.0008	4.0035	1.4	8.0	3.0233	3.8	25.4		5245.0

General mean = 5243.1 $cal_{20°}$ per gram weighed in air.
Maximum deviation from general mean = 1.9 calories.

and which are respectively 5242.4, 5242.0, 4251.3, 5237.4, cal. $_{15°}$ per gram weighed in air. The deviation of our mean results from theirs is just of the order of accuracy which can be expected with a Beckmann thermometer. (According to a private communication from the National Physical Laboratory a Beckmann thermometer can only be standardised to within 0.002°C. some thermo-chemists claim however that an accuracy of 0.001°C can be reached.) As Verkade has checked his own Beckmann thermometer against that of Roth and found both agreed very well with one another, it is to be expected that their values for the heat of combustion of a substance such as salicylic acid (the purification of which has been carried out beyond doubt to the utmost limits of refinement by such thermochemical experts) should be in very good agreement.

The ratios obtained by the above mentioned observers for the heat of combustion of benzoic acid to that of salicylic acid are given in the Table V in the order of increasing values.

TABLE V

Observer	Heat of combustion per gram in air in cal$_{20°}$		$\frac{\text{Benzoic acid}}{\text{Salicylic acid}}$
	Benzoic acid	Salicylic acid	
Swientoslawski	6329	5246.4	1.2063
Verkade	——	5246	1.2064
Roth	——	5245.3	1.2066
The authors	——	5243	1.2071
Berner	——	5241	1.2076

The Heat of Combustion of Meta and Para Hydroxybenzoic Acids

The samples supplied by Poulenc Frères showed signs of oxidation, and were therefore dissolved in boiling water, in presence of ignited animal charcoal, whilst passing in a current of sulphur dioxide. On filtering and cooling crystals separated and these were recrystallised from water, twice in the case of the meta and six times in the case of the para compound. (After many trials, water was found to be the best solvent). While, finely crystallised products were ultimately obtained, and these were dried over steam under reduced pressure. Table VI summarises the results.

The heats of combustion of o-, m-, and p-hydroxybenzoic acids are thus 5243.1 ±1.9, 5244.2 ±1.5, 5237.8 ±2.1 cal. 20° per gram weighed in air, whilst those found by Stohmann[1] in 1899 were respectively 5287, 5283 and 5260 calories.

This seems to indicate that at least some of the relatively large differences which are found in the literature between the heats of combustion of position isomers might be ascribed to insufficient purification and especially to inaccuracy of the calorimetric methods as used some thirty years ago.

[1] J. prakt. Chem., (2) **40**, 130, 150 (1889).

TABLE VI

No. of Expt.	Corrected wt. of substace in air	Temp. observed in calorimeter initial	final	Correc. in thousandths stem	stirring	Corrected rise in °C	Correction in calories for HNO_3	wool	C CO	Heat of combustion per gram
META—1	2.1572	0.9975	4.0005	1.7	7.8	3.0235	4.7	25.8	2.8	5245.0
2	2.1566	0.9990	4.0015	1.4	8.7	3.0224	4.0	25.0	1.6	5244.7
3	2.1565	0.9975	4.0010	1.9	10.0	3.0216	4.6	25.4	0.8	5242.7
4	2.1555	0.9970	3.9970	1.6	7.5	3.0209	4.6	25.0	2.0	5244.4

General mean = 5244.2 $cal_{20°}$ per gram weighed in air.
Maximum deviation from the general mean = 1.5 calories.

PARA—1	2.1561	0.9980	3.9990	1.8	9.5	3.0197	4.9	25.4		5239.9
2	2.1557	0.9913	3.9880	2.0	8.2	3.0165	4.6	25.4	2.6	5236.6
3	2.1546	1.0000	3.9960	1.2	8.2	3.0166	4.8	25.0		5238.4
4	2.1557	1.0055	4.0035	1.3	9.2	3.0175	5.2	26.5		5236.4
5	2.1561	1.0040	4.0025	0.7	9.5	3.0183	5.0	25.4		5237.5

General mean = 5237.8 $cal_{20°}$ per gram weighed in air.
Maximum deviation from general mean = 2.1 calories.

TABLE VII

No. of expt.	Corrected wt. of substance in air	Temp. observed in calorimeter initial	final	Correc. in thousandths stem	stirring	Corrected rise in °C	Correction in cal. for HNO_3	wool	C CO	Heat of combustion per gram.
Dextro										
1.	1.1900	0.9950	3.9960	2.6	7.0	3.0214	2.1	25.4		9501.6
2.	1.1900	1.0075	4.0080	3.1	6.5	3.0209	1.6	25.4		9500.5
3.	1.1901	0.9970	3.9975	2.2	8.0	3.0203	1.8	25.8	1.8	9487.7
4.	1.1904	0.9930	3.9910	1.2	6.0	3.0208	2.6	25.4	0.7	9496.7
5.	1.1904	1.0040	4.0080	1.2	9.8	3.0230	5.0	25.8		9501.7

General mean = 9499.4 $cal_{20°}$ per gram weighed in air.
Maximum deviation from the general mean = 2.7 calories.

Laevo										
1.	1.1900	0.9935	3.9935	2.0	6.8	3.0212	2.6	25.4	0.7	9501.2
2.	1.1901	0.9885	3.9880	1.8	5.2	3.0225	2.6	25.8		9503.5
3.	1.1907	1.0007	4.0035	1.3	6.7	3.0248	5.0	25.0		9504.8
4.	1.1901	0.9950	4.0000	1.4	9.6	3.0241	4.9	25.8		9506.6
5.	1.1899	1.0033	4.0065	1.3	8.5	3.0234	4.9	25.8	0.8	9506.7
6.	1.1901	1.0010	4.0035	1.7	8.5	3.0223	5.4	25.8		9500.6
7.	1.1901	0.9930	3.9965	2.2	8.7	3.0226	5.4	25.4		9501.8

General mean = 9503.6 $cal_{20°}$ per gram weighed in air.
Maximum deviation from general mean = 3.1 calories.

The Heat of Combustion of Dextro and Laevo Borneols

Both were obtained from the British Drug Houses and recrystallised several times from alcohol and then from heptane and finally dried by heating over an oil bath under reduced pressure.

The purification was continued until polarimetric measurements gave the constant molecular rotation $[\alpha]_D^{25} = +31^\circ$ and $[\alpha]_D^{25} = +38^\circ 7'$, using heptane as a solvent. The results obtained are shown in Table VII.

Summary

A. An adiabatic calorimeter with some new features has been described and this has given complete satisfaction.

2. With a mercury-in-glass thermometer, a greater precision in the measurement of heats of combustion is claimed as the result of the introduction of a new method consisting in selecting for all combustions almost exactly the same initial and final points on the Beckmann scale. This procedure giving a constant mean for the temperature of the calorimetric water, simplifies the calculations by rendering constant the otherwise variable correction for the specific heat of the water and of the metallic parts of the calorimeter.

It has also the great advantage of making all the readings independent of errors in the scale between the standardised points. With benzoic acid, for example, the maximum deviation from the general mean was thus improved from ±10 to ±1.6 calories.

3. The results obtained for the heats of combustion of naphthalene and salicylic acid show by their great concordance that both are very suitable as secondary standards for bomb calorimetry, although salicylic acid is perhaps slightly better owing to its lower volatility.[1]

4. The consideration of the heats of combustion of the ortho-meta- and para-hydroxy derivatives of benzoic acid leads to the conclusion that the energy contents of the ortho and meta derivatives are the same within the limits of experimental error, whilst a very slight difference, of the order of about three times the experimental error, is indicated in the case of the para compound as compared to the ortho- and meta-isomers.

5. The values obtained for the two optically active forms of borneol show that there is no energy change involved in the transformation of the one form into the other.

The authors wish to thank Professor E. C. C. Baly F. R. S. for the facilities he has kindly placed at their disposal for carrying out this work. They feel also greatly indebted to Professor Bannister for the bomb he has kindly lent to them.

The University,
Liverpool,
England.
July 1, 1926.

[1] Verkade: Rec. Trav. chim., **44**, 799 (1924).

THE MASS UNIT OF THE CHEMICAL POTENTIAL

BY WILDER D. BANCROFT

It may be carrying coals to Newcastle to explain selected passages from Gibbs to the chemists; but I have found no chemists—either hand-picked or run-of-mine—who would explain them to me and consequently I feel temporarily like a discoverer, quite regardless of whether I am one or not. For the sake of convenience the references are to the first volume of "The Collected Papers of J. Willard Gibbs," edited by H. A. Bumstead and R. G. Van Name.

"If we consider the amount and kind of matter in a homogeneous mass as fixed, its energy is a function of its entropy η, and its volume v and the differentials of these quantities are subject to the relation

$$d\epsilon = td\eta - pdv, \qquad (11)$$

t denoting the (absolute) temperature of the mass, and p its pressure. For $td\eta$ is the heat received, and pdv the work done by the mass during its change of state. But if we consider the matter in the mass as variable, and write $m_1, m_2, \ldots m_n$ for the quantities of the various substances $S_1, S_2, \ldots S_n$ of which the mass is composed, ϵ will evidently be a function of η, v, m_1, $m_2, \ldots m_n$, and we shall have for the complete value of the differential of ϵ

$$d\epsilon = td\eta - pdv + \mu_1 dm_1 + \mu_2 dm_2 \ldots + \mu_n dm_n, \qquad (12)$$

$\mu_1, \mu_2, \ldots \mu_n$ denoting the differential coefficients of ϵ taken with respect to $m_1, m_2, \ldots m_n$.

"The substances $S_1, S_2, \ldots S_n$, of which we consider the mass composed, must of course be such that the values of the differentials $dm_1, dm_2, \ldots dm_n$ shall be independent, and shall express every possible variation in the composition of the homogeneous mass considered, including those produced by the absorption of substances different from any initially present. It may therefore be necessary to have terms in the equation relating to component substances which do not initially occur in the homogeneous mass considered, provided, of course, that these substances, or their components, are to be found in some part of the whole given mass.

"If the conditions mentioned are satisfied, the choice of the substances which we are to regard as the components of the mass considered may be determined entirely by convenience, and independently of any theory in regard to the internal constitution of the mass. The number of components will sometimes be greater, and sometimes less, than the number of chemical elements present. For example, in considering the equilibrium in a vessel containing water and free hydrogen and oxygen, we should be obliged to recognize three components in the gaseous part. But in considering the equilibrium of dilute sulphuric acid with the vapor which it yields, we should have only two components in the liquid mass, sulphuric acid (anhydrous, or of any particular degree of concentration) and (additions) of water. If, however, we are considering sulphuric acid in a state of maximum concentra-

tion in connection with substances which might possibly afford water to the acid, it must be noticed that the condition of the independence of the differentials will require that we consider the acid in the state of maximum concentration as one of the components. The quantity of this component will then be capable of variation both in the positive and in the negative sense, while the quantity of the other component can increase but cannot decrease beyond the value zero.

"For brevity's sake, we may call a substance S_a an *actual component* of any homogeneous mass, to denote that the quantity m_a of that substance in the given mass may be either increased or diminished (although we may have so chosen the other component substances that $m_a = 0$); and we may call a substance S_b a *possible component* to denote that it may be combined with, but cannot be subtracted from the homogeneous mass in question. In this case, we must so choose the component substances that $m_b = 0$.

"The units by which we measure the substances of which we regard the given mass as composed may each be chosen independently. To fix our ideas for the purpose of a general discussion, we may suppose all substances measured by weight or mass. Yet in special cases, it may be more convenient to adopt chemical equivalents as the units of the component substances," p. 63.

"If we call a quantity μ_x, as defined by such an equation as (12), the potential for the substances S_x in the homogeneous mass considered, these conditions may be expressed as follows—*The potential for each component substance must be constant throughout the whole mass,*" p. 65.

"Whenever, therefore, each of the different homogeneous parts of the given mass may be regarded as composed of some or all of the same set of substances, no one of which can be formed out of the others, the condition which (with equality of temperature and pressure) is necessary and sufficient for equilibrium between the different parts of the given mass may be expressed as follows:—

"*The potential for each of the component substances must have a constant value in all parts of the given mass of which that substance is an actual component, and have a value of not less than this in all parts of which it is a possible component,*" p. 67.

"In the definition of the potentials μ_1, μ_2, etc., the energy of a homogeneous mass was considered as a function of its entropy, its volume, and the quantities of the various substances composing it. Then the potential for one of these substances was defined as the differential coefficient of the energy taken with respect to the variable expressing the quantity of that substance. Now as the manner in which we consider the given mass as composed of various substances is in some degree arbitrary, so that the energy may be considered as a function of various different sets of variables expressing quantities of component substances, it might seem that the above definition does not fix the value of the potential of any substance in the given mass, until we have fixed the manner in which the mass is to be considered as composed. For example, if we have a solution obtained by dissolving in water a certain salt containing

water of crystallization, we may consider the liquid as composed of m_S weight units of the hydrate and m_W of water or as composed of m_s of the anhydrous salt and m_w of water. It will be observed that the values of m_S and m_s are not the same, nor those of m_W and m_w, and hence it might seem that the potential for water in the liquid considered as composed of the hydrate and water, viz.,

$$\left(\frac{d\epsilon}{dm_W}\right)_{\eta,\ v,\ m_S},$$

would be different from the potential for water in the same liquid considered as composed of anhydrous salt and water, viz.,

$$\left(\frac{d\epsilon}{dm_w}\right)_{\eta,\ v,\ m_s},$$

The value of the two expressions is, however, the same, for, although m_W is not equal to m_w, we may of course suppose dm_W to be equal to dm_w, and then the numerators in the two fractions will also be equal, as they each denote the increase of energy of the liquid, when the quantity dm_W or dm_w of water is added without altering the entropy and volume of the liquid. Precisely the same considerations will apply also to any other case. In fact, we may give a definition of a potential which shall not presuppose any choice of a particular set of substances as the components of the homogeneous mass considered.

"*Definition.*—If to any homogeneous mass we suppose an infinitesinal quantity of any substance to be added, the mass remaining homogeneous and its entropy and volume remaining unchanged, the increase of the energy of the mass divided by the quantity of the substance added is the *potential* for that substance in the mass considered. (For the purposes of this definition, any chemical element or combination of elements in given proportions may be considered a substance, whether capable or not of existing by itself as a homogeneous body," p. 92.

"Between the potentials for different substances in the same homogeneous mass the same equations will subsist as between the units of these substances. That is, if the substances, S_a, S_b, etc. S_k, S_l, etc., are components of any given mass, and are such that

$$\alpha S_a + \beta S_b + \text{etc.} = \kappa S_k + \lambda S_l + \text{etc.}, \qquad (120)$$

S_a, S_b, etc., κ, λ, etc., denoting numbers, then if μ_a, μ_b, etc., μ_k, μ_l, etc., denote the potentials for those substances in the homogeneous mass.

$$\alpha\mu_a + \beta\mu_b + \text{etc.} = \kappa\mu_k + \lambda\mu_l + \text{etc.} \qquad (121)$$

To show this, we will suppose the mass considered to be very large. Then the first member of (121) denotes the increase of the energy of the mass produced by the addition of the matter represented by the first member of (120), and the second member of (121) denotes the increase of energy of the same mass produced by the addition of the matter represented by the second member of (120) the entropy and volume of the mass remaining unchanged in each case. Therefore, as the two members of (120) represent the same matter in kind and quantity, the two members of (121) must be equal.

"But it must be understood that equation (120) is intended to denote equivalence of the substances represented *in the mass considered*, and not merely chemical identity; in other words, it is supposed that there are no passive resistances to change in the mass considered which prevent the substances represented by one member of (120) from passing into those represented by the other. For example, in respect to a mixture of vapor of water and free hydrogen and oxygen (at ordinary temperature), we may not write

$$9\,S_{Aq} = 1\,S_H + 8S_O$$

but water is to be treated as an independent substance, and no necessary relation will subsist between the potential for water and the potentials for hydrogen and oxygen," p. 94.

If we work at temperatures at which the reaction of hydrogen and oxygen to form water is a reversible one or if we produce a state of reversible equilibrium by the addition of a suitable catalytic agent (pp. 139, 141, 184), then we can write

$$9S_{Aq} = 1\,S_H + 8S_O$$

or

$$9\mu'_{Aq} = 1\mu'_H + 8\mu'_O.$$

Gibbs says, p. 363, that "when the proximate components of a gas-mixture are so related that some of them can be formed out of others, although not necessarily in the gas-mixture itself at the temperatures considered, there are certain phases of the gas-mixture which deserve especial attention. There are the *phases of dissipated energy*, i.e., those phases in which the energy of the mass has the least value consistent with its entropy and volume. An atmosphere of such a phase could not furnish a source of mechanical power to any machine or chemical engine working within it, as other phases of the same matter might do. Nor can such phases be affected by any catalytic agent. A *perfect catalytic agent* would reduce any other phase of the gas-mixture to a phase of dissipated energy. The condition which will make the energy a minimum is that the potentials for the proximate components shall satisfy an equation similar to that which expresses the relation between the units of weight of these components. For example, if the components were hydrogen, oxygen, and water, since one gram of hydrogen with eight grams of oxygen are chemically equivalent to nine grams of water, the potentials for these substances in a phase of dissipated energy must satisfy the relation"

$$9\mu'_{Aq} = 1\mu'_H + 8\mu'_O$$

If we express these units in gram-molecular weights, as chemists usually do, we shall write for a phase of dissipated energy, which is another way of saying a state of reversible equilibrium,

$$2\mu_{H_2O} = \mu_{H_2} + \mu_{O_2}$$

where μ' is the chemical potential referred to grams and μ the chemical potential referred to molecular weights. In order to avoid confusion, Lash Millor suggests using the words specific potential for the chemical potential referred to grams, the molecular potential (or mol-potential) for the chemical potential referred to molecular weights, and the equivalent potential for the

chemical potential referred to equivalent weights. The coulomb potential might be used for the chemical potential referred to the electrochemical equivalent.

This is a bit puzzling to the chemist, especially if he wishes to deduce the mass law from the relation between the potentials at equilibrium. The difficulty is due to the fact that Gibbs defines the chemical potential in a purely formal way.

"The potential for any substance in any homogeneous mass is equal to the amount of mechanical work required to bring a unit of the substance by a reversible process from the state in which its energy and entropy are both zero into combination with the homogeneous mass, which at the close of the process must have its original volume, and which is supposed so large as not to be sensibly altered in any part. All other bodies used in the process must by its close be restored to their original state, except those used to supply the work, which must be used only as the source of the work. For, in a reversible process, when the entropies of other bodies are not altered, the entropy of the substance and mass taken together will not be altered. But the original entropy of the substance is zero; therefore the entropy of the mass is not altered by the addition of the substances. Again, the work expended will be equal to the increment of the energy of the mass and substance taken together, and therefore equal, as the original energy of the substance is zero, to the increment of energy of the mass due to the addition of the substance, which by the definition on p. 93 is equal to the potential in question," p. 95.

Under this definition the potential of any given substance is a function of the mass unit adopted. The molecular chemical potential or the chemical potential of a gram-molecular weight of oxygen taken as the mass unit is thirty-two times of the specific chemical potential or the potential of the same amount of oxygen with one gram taken as the mass unit. In other words $\mu_{H_2} = 2\mu'_H$, $\mu_{O_2} = 32\mu'_O$ and $\mu_{H_2O} = 18\mu'_{Aq}$. Substituting these values in the equation $2\mu_{H_2O} = 2\mu_{H_2} + \mu_{O_2}$, we get $36\mu'^{Aq} = 4\mu_H + 32\mu_O$ or $9\mu'_{Aq} = 1\mu'_{Hy} + 8\mu'_{Ox}$.

Lash Miller points out that when hydrogen, oxygen and water are in a state of reversible equilibrium, the following three equations all say exactly the same thing:—

9× specific potential water = 8× specific potential oxygen
+ specific potential hydrogen
2× molecular potential water = molecular potential water
+ 2× molecular potential hydrogen
Equivalent potential water = equivalent potential oxygen
+ equivalent potential hydrogen.

All these equations are identical under the formal definition of the potential. The question then arises whether this definition is a desirable one in the general form which Gibbs has given it. I have not yet found that Gibbs has discussed this question definitely anywhere. Really the mass unit to be taken for the chemical potential should be the one which is the chemical unit for the process under consideration, because this is the one which leads

directly to the mathematical formulas describing the equilibria. When we are considering pressure-volume-temperature relations for gases, the obvious units are the molecular weights. Ignoring variations from the gas law, two grams of hydrogen are equivalent to thirty-two grams of oxygen, eighteen grams of water, or thirty-six and a half grams of hydrochloric acid. So far as I can see, it is quite impossible to pass directly from the relation $9\mu'_{Aq} = 1\mu'_{Hy} + 8\mu'_{Ox}$ to the equation $KC^2_{H_2O} = C^2_{H_2} . C_{O_2}$. We must pass through the relation $2\mu_{H_2O} = 2\mu_{H_2} + \mu_{O_2}$. When considering mass law relations, we must, therefore, refer the chemical potentials to the molecular weights as units. Gibbs actually does this, p. 362, and assumes that we shall follow him.

"From the physical properties which we attribute to ideal gases, it is easy to deduce their fundamental equations. The fundamental equation in ϵ, η, v and m for an ideal gas is

$$c \log \frac{\epsilon - Em}{cm} = \frac{\eta}{m} + H + a \log \frac{m}{v}; \qquad (17)$$

that in ψ, t, v, and m is

$$\psi = Em + mt\,(c - H - c \log t + a \log m/v. \qquad (18)$$

that in p, t and μ is

$$p = ae^{\frac{H-c-a}{a}} t^{\frac{c+a}{a}} e^{\frac{\mu - E}{at}} \qquad (19)$$

where e denotes the base of the Naperian system of logarithms. As for the other constants, c denotes the specific heat of the gas at constant volume, a denotes the constant value of $pv \div mt$, E and H depend upon the zeros of energy and entropy. The two last equations may be abbreviated by the use of different constants. The properties of fundamental equations mentioned above may easily be verified in each case by differentiation.

"The law of Dalton respecting a mixture of different gases affords a point of departure for the discussion of such mixtures and the establishment of their fundamental equations. It is found convenient to give the law the following form:—

"*The pressure in a mixture of different gases is equal to the sum of the pressures of the different gases as existing each by itself at the same temperature and with the same value of its potentials.*"

If we take the logarithm of equation (19) and consider the temperature as constant, we get

$$\mu = at \log p + \text{constant}$$

which is identical with the one that the modern physical chemist would write,

$$\mu = RT \log p + C.$$

If we express the chemical potentials in terms of molecular weights, as mass units, the relation for the reversible equilibrium between hydrogen, oxygen, and water becomes $2\mu_{H_2} + \mu_{O_2} = 2\mu_{H_2O}$

or, in terms of pressures,

$$2\,RT \log p_1 + 2\,C_1 + RT \log p_2 + 2 \log C_2 = 2\,RT \log p_3 + 2\,C_3,$$

which reduces to $p_1^2 . p_2 = Kp_3^2$,

the regular mass law equation for this case.

If we are dealing with electromotive forces, Gibbs has shown that the electromotive force of a reversible cell is a measure of the difference of the chemical potentials. If we take the gram as the mass unit, the electromotive force is proportional to the difference of the specific chemical potentials. If we take the electrochemical equivalent as the mass unit, the electromotive force is equal to the difference of the coulomb chemical potentials, p. 331.

"We know by experience that in certain fluids (electrolytic conductors) there is a connection between the fluxes of the component substances and that of electricity. The quantitative relation between these fluxes may be expressed by an equation of the form

$$De = \frac{Dm_a}{\alpha_a} + \frac{Dm_b}{\alpha_b} + \text{etc.} - \frac{Dm_g}{\alpha_g} - \frac{Dm_h}{\alpha_h} + \text{etc.}, \qquad (682)$$

where De, Dm_a, etc. denote the infinitesimal quantities of electricity and of the components of the fluid which pass simultaneously through any same surface, which may be either at rest or in motion, and α_a, α_b, etc., α_g, α_h, etc. denote positive constants. We may evidently regard Dm_a, Dm_b, etc., Dm_g, Dm_h, etc. as independent of one another. For, if they were not so, one or more cou'd be expressed in terms of the others and we could reduce the equation to a shorter form in which all the terms of this kind would be independent.

"Since the motion of the fluid as a whole will not involve any electrical current, the densities of the components specified by the suffixes must satisfy the relation.

$$\frac{\gamma_a}{\alpha_a} + \frac{\gamma_b}{\alpha_b} + \text{etc.} = \frac{\gamma_g}{\alpha_g} + \frac{\gamma_h}{\alpha_h} + \text{etc.} \qquad (683)$$

These densities, therefore, are not independently variable, like the densities of the components which we have employed in the other cases.

"We may account for the relation (682) by supposing that electricity (positive or negative) is inseparably attached to the different kinds of molecules, so long as they remain in the interior of the fluid, in such a way that the quantities α_a, α_b, etc. of the substances specified are each charged with a unit of positive electricity, and the quantities α_g, α_h, etc. are each charged with a unit of negative electricity. The relation (683) is accounted for by the fact that the constants α_a, α_g, etc. are so small that the electrical charge of any sensible portion of the fluid varying sensibly from the law expressed in (683) would be enormously great, so that the formation of such a mass would be resisted by a very great force.

"It will be observed that the choice of the substances which we regard as the components of the fluid is to some extent arbitrary and that the same physical relations may be expressed by different equations of the form (682), in which the fluxes are expressed w th reference to different sets of components. If the components chosen are such as represent what we believe to be the actual molecular constitution of the fluid, those of which the fluxes appear in the equation (682) are called the *ions* and the constants of the equation are called their *electro-chemical equivalents*. For our present purpose, which

has nothing to do with any theories of molecular constitution, we may choose such a set of components as may be convenient, and call those *ions*, of which the fluxes appear in the equation of the form (682) without farther limitation."

When we let V′, V″ denote the electrical potentials in pieces of the same metal connected with the two electrodes of a reversible cell, "when the great effect of gravity may be neglected and when there are but two electrodes, as in a galvanic or electrolytic cell, we have for any cation

$$V'' - V' = \alpha_a (\mu_\alpha' - \mu_\alpha'') \qquad (687)$$

and for any anion

$$V'' - V' = \alpha_g (\mu_g'' - \mu_g') \qquad (688)$$

where V″−V′ denotes the electromotive force of the combination. That is:—

"When all the conditions of equilibrium are fulfilled in a galvanic or electrolytic cell, the electromotive force is equal to the difference in the values of the potential for any ion or apparent ion at the surfaces of the electrodes multiplied by the electrochemical equivalent of that ion, the greater potential of an anion being at the same electrode as the greater electrical potential, and the reverse being true of a cation," p. 332.

Gibbs thus states explicitly that we can refer the chemical potentials to grams or to electrochemical equivalents and that the second is simpler because then equations (687) and (688) become

$$V''-V' = (\mu)_\alpha' - (\mu)_\alpha'' \text{ and } V''-V' = (\mu)_g'' - (\mu)_g'.$$

Actually, we do not use either of these expressions, because we are concerned with the osmotic pressure of the ions and consequently we refer the chemical potentials to gram ions and bring the valence of the ion in elsewhere in the formula. This gives $nF(V'' - V') = (\mu)' - (\mu_a)'' = (\mu)_g'' - (\mu)_g'$. For the single potential difference at the surface of an electrode reversible with respect to the cation, this becomes

$$nFE = \mu_m - \mu_s = RT \log P/p,$$

which is the Nernst equation, μ_m being the potential of the metal and μ_s the potential of the cation in solution.

The measurement of an electromotive force, as usually carried out, does not involve the measurement or knowledge of the current in any portion of the apparatus, except that there must be no current flowing through the telephone, galvanometer, or electrometer. Since the value of the coulomb chemical potential will depend on the value assumed for the coulomb, it may seem to some that the electromotive force, which is apparently independent of the value of the coulomb cannot necessarily be a measure of the coulomb chemical potential. This is an error, because the value of the ampere (coulomb per second), the volt, and the ohm are so connected by Ohm's law that we have only two independent variables. If we keep the ohm constant and vary the value of the coulomb, we shall necessarily change the value of the volt. While it might be possible on paper to keep the unit of potential difference constant and to vary simultaneously the ohm and the coulomb, this is not practical, however, because we have a relation between the joule (volt-coulomb) and the calorie, so that we cannot very well vary the coulomb

without varying the volt. Actually, this discussion is academic because nobody has any intention of doubling or halving the value of the coulomb.

It may be asked what the use of this whole paper is when Gibbs has already stated clearly that the chemical potential may be referred to any mass unit, meaning thereby that in equations one may use specific potentials, molecular potentials, etc., provided one introduces in each case the appropriate factors. One reason for writing this paper is that Ostwald has apparently never been clear on the question of the mass unit and it is probable that others have been equally confused. I know that I have been.

In an early paper Ostwald[1] gives the combining weight as the capacity factor of chemical energy and says that "the capacity factor of the chemical energy, like that of heat is proportional to the mass and the weight. From the name for it, the combining weight, one must not conclude that the chemical capacity is fundamentally a weight. It is not that any more than it is a mass. It is only proportional to these two and the proportionality factor changes with the nature of the substance. A 'dimension' in the usual units of length, time, and mass can no more be given for the capacity factor of chemical energy than for any of the other energy factors of the table; all assumptions to the contrary rest on arbitrary omissions and therefore on error."

A little later there is a paragraph[2] which may or may not have a bearing. "It must finally be mentioned that several capacity factors are equal for chemically comparable amounts of different substances. This was first suggested by LeChatelier and was emphasized strongly by Meyerhoffer[3]. Thus the value R of the gas equation PV = RT is the same for molecular amounts, the heat capacity for atomic weights, and the electrochemical capacity for equivalent weights. These three examples show, however, that the weights in question are not proportional from case to case, for the gas content, the heat capacity, and the electrochemical capacity are proportional respectively to the molecular weight, the atomic weight, and the electrochemical equivalent, and these are not in general proportional for different substances. Other capacities, such as the mass, do not show the relation and consequently the rule is by no means general."

On page 500 of the same volume, Ostwald says: "While the intensity factor of heat, the temperature, is well known to us and the other factor, the entropy, is difficult to grasp, the converse is true in the case of the chemical energy. It appears to us so obvious that the chemical energy is proportional to the amount of the substances in question, other things being equal, that at first we do not trouble to formulate such a hypothesis. Nevertheless, it is necessary to be clear that this proportionality of chemical energy to mass and weight is an empirical fact, not in any way necessary *a priori*. Mass is a magnitude which belongs only in the field of kinetic energy and is connected with chemical energy only through this proportionality law. This latter holds

[1] Z. physik. Chem., **10**, 370 (1892).
[2] Lehrbuch allgem. Chemie, **2** I, 50 (1893).
[3] Z. physik. Chem., **7**, 544 (1891).

also for weight. In addition, we know from experience that the proportionality factor depends to a great extent on the special (chemical) nature of the substances.

"The factor of the chemical energy which is proportional to the mass of the substances in question, does not have the character of an intensity because it determines neither the occurrence nor the form of the chemical changes. We shall, therefore, have to set the chemical capacity proportional to the mass. It is not desirable to make the proportionality factor between the mass and the chemical capacity equal to unity and thus refer the chemical energy to the unit of mass of the different substances as happened in the earlier development of thermochemistry. The law of combining weights suggests to us to multiply the values referred to the unit of mass by combining weights and thereby to evaluate the chemical energy for such quantities of different substances which stand in the ratio of the combining weights. In this way the necessary calculations are reduced to a minimum and the relations between the chemical energy of different substances are easier to see."

On p. 502 Ostwald says: "In regard to the choice of the chemical capacity factor we have to make a definite, more or less arbitrary, agreement, just as we had to do in regard to the chemical combining weights. In that case it was possible so to determine these latter values that a number of other relations assume a simple and clear form, whereby a definite system of values, the atomic weights now in use, have proved the most serviceable in every way. Since the numerical values of the chemical capacity factors have no other condition to satisfy than that their sum for the substances and the amounts of the substances shall be equal on both sides of a chemical equation for the reaction, a condition which the atomic and combining weights satisfy, *we may take these values as the units of the chemical capacity for the different substances.*"

All this is a bit vague, but it seems to mean that the combining weights are the mass units for the chemical capacity factor. This does not seem to me to be right at all. Gibbs has shown that in a completely reversible voltaic cell the electromotive force is a measure of the chemical potential (or rather of the difference of chemical potential) when we take as the mass unit the electrochemical equivalent, which is quite a different thing from the equivalent weight, the latter being approximately 96500 times the former. On the other hand, we must take the molecular weights as the mass units if we are to deduce the mass law directly from the relation between the chemical potentials at equilibrium.

At first sight this seems to make the choice of the mass units an entirely arbitrary one; but I think that this is not the case, and Ostwald has himself shown the way out, apparently without realizing it. The difficulty is in the Gibbs definition of the potential, p. 93. "If to any homogeneous mass we suppose an infinitesimal quantity of any substance to be added, the mass remaining homogeneous and its entropy and volume remaining unchanged, the increase of the energy of the mass divided by the quantity of the substance added is the *potential* for that substance in the mass considered."

This definition is absolutely right; but, as Ostwald[1] has pointed out, we cannot determine the absolute value of the chemical potential of any substance because we do not know the change of the energy with the change of mass. All we can do is to measure differences of chemical potential. As I see it, this means that we are always measuring the chemical potential of a reaction and that consequently we must use the mass units of the reaction. If we are making electrometric measurements the unit is the mass associated with the unit quantity of electricity, the coulomb in electrochemical work. If we are studying pressure relations in a gas or a solution, the unit is the molecular weight of the substance or the ion as the case may be.

I have thought that the electromotive force was a measure of the chemical potential of the system and that there should be a chemical potential for any organic compound if we could only measure it. It is now clear that this was a mistaken point of view. Since we measure only the difference of chemical potential for a given reaction, there are really as many chemical potentials in an organic compound as there are bonds which can be broken. It is these values which must be measured some day.

Another reason for writing this article is that we do not yet make the use of the chemical potential in chemistry that I am sure we ought to make. It seems probable that this is due in part to our misconceptions of the chemical potential. Gibbs deduced the phase rule from the relation among the potentials, and Lash Miller has made use of it to a limited extent in discussing changes of solubility, and it is recognized that electromotive force determinations measure differences of chemical potential; but that is about as far as we go.

Guldberg and Waage deduced the mass law from assumptions in regard to reaction velocity and Gibbs deduced the mass law from the relation between the potentials at equilibrium; but no one, so far as I know, has ever deduced the reaction velocity formulas from the chemical potentials, though Nernst has suggested that the reaction velocity may be proportional to the difference of chemical potential divided by the unknown chemical resistance. Of course one can substitute from one set of equations to the other. If we consider the reacting substances as present in equivalent quantities, we can write for monomolecular, bimolecular, and trimolecular reactions the equations $d\mu/dt = R$, $d\mu/dt = R(A-x)$ and $d\mu/dt = R(A-x)^2$ respectively; or for the general case $d\mu/dt = k\,(A-x)^{n-1}$ where n is the order of the reaction; but we cannot deduce these equations and they are not what we want anyhow. By subtraction, one can also write the general equation $\frac{dx}{dt} = \epsilon \frac{\mu_1 + \mu_2 \ldots \mu_n}{R}$, which is of no value until we can deduce it and show that this is the necessary formula and that has not yet been done. Consequently, a further study of the chemical potential is essential.

I feel sure also that some day the history of chemistry will be written as showing the development (conscious and unconscious) of the theory of the

[1] Lehrbuch allgem. Chemie, **2** II, 123 (1902).

chemical potentials; but we are certainly a long way from that still. I hope that this article may stimulate somebody better qualified than I am, and that it will thereby bring that day nearer.

The general conclusions of this paper are:—

1. We never measure any absolute chemical potential but only the difference of potential due to some reaction.

2. The chemical potentials may be referred to any mass units; but general relations are brought out more clearly if the mass units appropriate to the reaction used.

3. When we are studying reactions involving the pressures of gases or the osmotic pressures of solutions, the appropriate mass units are the molecular weights of the reacting substances or ions.

4. If one is studying electrochemical reactions, the appropriate mass units are the electrochemical equivalents, the masses which are transferred with one coulomb. These are equal to the equivalent weights divided by the Faraday constant.

5. Nobody has worked out what the appropriate mass units are in the case of electrical endosmose or of frictional electricity.

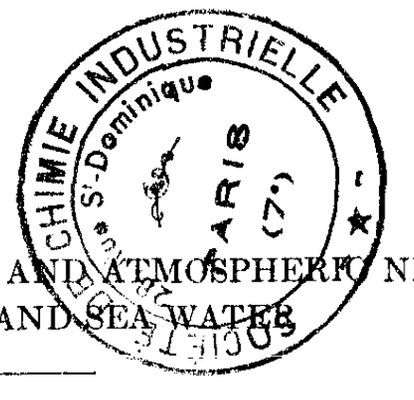
6. In the case of organic compounds one can have as many chemical potentials as there are bonds which can be broken or activated.

7. The mass law equations have been deduced from the reaction velocity equations and from the relations between the chemical potentials; but apparently nobody has deduced the reaction velocity equations from the relations between the potentials although the difference of chemical potential must be one of the factors determining the reaction velocity, and in spite of the fact that Ohm's law holds absolutely for reactions taking place under certain clearly-defined conditions.

8. The history of chemistry will undoubtedly be written some day as a study of the conscious and unconscious development of the theory of the chemical potential.

Cornell University.

Q-17 81



ON THE SOLUBILITY OF PURE AND ATMOSPHERIC NITROGEN IN DISTILLED AND SEA WATER

BY J. H. COSTE

The solubility of nitrogen in pure water has been investigated by several workers whose results are not very concordant. The case of sea water with its varying salt content has been studied by some of these workers with still less satisfactory agreement.

A very useful critical survey of then available data was made in 1886 by Hamberg[1] who wrote

"Da ich während der Expedition des Freih. von Nordenskiöld, 1883, ein kleines Material von Bestimmungen des Stickstoffgases in Meerwasser gesammelt hatte, musste ich zu deren Verwerthung einige Normalbestimmungen haben um sie damit zu vergleichen. Je mehr ich in die Kritik von Bunsen's, Dittmar's und Tornoë's Bestimmungen hineinkam, desto mehr wurde ich überzeugt, dass diese ganze Frage einer Revision bedürfe. Unter anderem hielt ich es fur nothwendig, nicht nur die Wirkung der Temperatur, sondern auch die des Salzgehaltes auf die Menge des Stickstoffgases zu untersuchen."

Notwithstanding the considerable amount of work which has been done since 1886 those who need exact data will, like Hamberg, conclude that the whole question needs revision. In the following I have tried to discuss and collate the data available .

The Effect of Argon on the Solubility of Atmospheric Nitrogen

The complication introduced by argon in absorptiometric determinations of the solubility of nitrogen seem first to have been realised by C. J. Fox[2] who, in 1907, discussed the question and deduced an expression for evaluing the error due to the greater solubility of argon than nitrogen. Bohr and Bock[3] and Winkler[4] in 1891 were unaware of the existence of argon, which was discovered in 1894. Winkler,[5] in 1901, referred to his work as being on atmospheric nitrogen and in a foot-note said "Unter atmosphärischem Stickstoff soll der, aus Luft dargestellte, Argon u. s. w. haltige Stickstoff verstanden werden." He does not seem to have realised that an error was thereby introduced into his results. The error is peculiar to the absorptiometric method in which a finite volume of water is agitated with a small, finite volume of gas. The

[1] Hamberg: J. prakt. Chem., **33**, 433 (1886). "Beitrage zur Chemie des Meerwassers."

[2] C. J. J. Fox: "On the Coefficients of Absorption of Nitrogen and Oxygen in Water and Sea Water and of Atmospheric Carbonic Acid in Sea Water." *Trans. Faraday Soc.*, **5**, 68, (1909) and Internat. Hydrog. Comm. Publication de Circonstance, No. 41 (1907).

[3] Ch. Bohr and J. Bock: Wied. Ann., **44**, 318 (1891). "Bestimmung der Absorption einiger Gase in Wasser bei den Temperaturen zwischen 0° und 100°."

[4] L. W. Winkler: Ber. **24**, 3602 (1891). "Löschlichkeit der Gase in Wasser."

[5] L. W. Winkler: Ber., **34**, 1408 (1901).

presence in the gas of two constituents of varying solubilities leads to the final equilibrium being obtained between water and a gas containing less of the more soluble than the original mixture. Two definite values may be desired, either the solubility of atmospheric nitrogen α' or that of pure nitrogen α_N. What is actually found in the absorptiometric experiment is something between the two, α. Of these three values, a' is the highest.

Fox gives an expression for the value of $\alpha' - \alpha$ in any absorptiometric experiment in which the composition of the gas experimented with, and the ratio of volumes of gas to water = k are known. Substituting the proper numerical values and using α_A at 0° = 0.0578 and α_N at 0° = 0.0230 (Fox) we get

$$\alpha' - \alpha = 0.00001418/k + 0.0582$$

k = volume of residual gas/volume of liquid. A few values of 1000 $(\alpha' - \alpha)$ which will be the correction in millilitres of gas for a litre of liquid are given below.

k = 0	.1	.2	.5	1.0	10
1000 $(\alpha' - \alpha)$ = 0.1243	0.09	0.05	0.02	0.01	0.001
Percentage error 1.06	0.39	0.22	0.09	0.04	0.004

In actual working the error would never reach the maximum value nor fall as low as the lowest given, since one could not use an experiment in which all the gas was absorbed nor measure with sufficient accuracy a volume of gas many times that of the liquid. It will be noted however that in the method of working by saturation of the liquid with an unlimited volume of gas and boiling off or pumping out the gas $\alpha' - \alpha = 0$ that is the true absorption coefficient of the gaseous mixture is obtained. What, however, is the absorption coefficient of the pure gas, nitrogen = N_2?

Fox shows, and indeed it is obvious, that

$$\alpha_N = \alpha' - 0.01185\alpha_A/0.098815$$

[0.01185 and 0.98815 being respectively the volumes of argon and nitrogen in one volume of atmospheric nitrogen]. Since α_A = about 2.45α and α'/α_N we can simplify this to

$$\alpha_N = 0.9827\ \alpha'$$

with an error of not more than, say, 1/1000. We see therefore that the error, due to argon of an absorptiometric experiment cannot exceed 1% of the value determined and that the difference between the true values for N_2 and atmospheric nitrogen is about 100 (1 − .9827) or say 1.7 percent within a wide range of temperature. We can now consider actual results.

Atmospheric Nitrogen in Distilled Water

Table I shows the results obtained by various workers from Bunsen down to Fox.

TABLE I

One litre of distilled water absorbs from atmospheric nitrogen at a pressure of 760 mm + tension of aqueous vapour millilitres of the mixed gas according to

At a temperature of 0°C	Bunsen	Dittmar	Hamberg	Bohr and Bock	Winkler	Fox
0	20.35	24.40	24.21	(23.88)	23.54	23.59
+5	17.94	21.62	21.42	(21.53)	20.86	21.03
10	16.07	19.43	19.15	(19.56)	18.61	18.95
15	14.78	17.65	17.37	(17.86)	16.85	17.31
20	14.03	16.18	15.98	(16.39)	15.45	15.98
25	——	14.95	14.94	(15.04)	14.34	14.89

Bunsen's[1] results are clearly inaccurate. As I wrote in 1918 his "work stands *alone as that of a pioneer and cannot be criticized like that of other workers.*"[2]

Dittmar[3] was a careful worker but I am inclined to think that there were too many unprotected rubber joints in his apparatus. Most of his results are distinctly higher than those of the others. Hamberg saturated water with air and used a very good gas-extraction and gas-measuring apparatus. He considered air to contain 79.05% of the mixture he called nitrogen. Neither his results or Dittmar's are affected by error due to argon since in a bubbling process of saturation k is very large. Bohr and Bock used both absorptiometric and boiling-out methods but their results are not easily amenable to correction. Winkler's absorptiometric results given in Table I are not those he published but are corrected for the value of k which was fairly constant at 1/4. The figures are taken from Landolt and Börnstein, Fifth edition, p. 765, Table 131b (1923). I have satisfied myself that the corrections are of the order required by Fox's expression. Fox's values are those given in Landolt and Börnstein and calculated from his values for the "nitrogen" in air. It will be seen that above 5° Hamberg and Fox agree well and the following rounded figures are probably fairly trustworthy.

One litre of water at	10°	15°	20°	25°C
dissolves	19.0	17.3	16.0	14.9ml.

of atmospheric nitrogen.

The disagreement between various workers at the lower temperatures is very remarkable. I note that the only tables given now in Landolt and Börnstein are Winkler's and Fox's, recalculated as above mentioned.

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[1] R. Bunsen: "Gasometry" (Trans. H. Roscoe, 1857).

[2] J. H. Coste: J. Soc. Chem. Ind., **36**, 846 (1917). The "Absorption of Atmospheric Gases by Water."

[3] W. Dittmar: "The Challenger Expedition, Report on Chemistry and Physics."

Pure Nitrogen in Distilled Water

The only persons who appear to have determined directly the solubility of N_2 in water are Braun[1] and Adeney and Becker.[2] Adeney and the late H. G. Becker published a few values incidentally in one of their papers on the rates of absorption. All the other workers used "nitrogen" from air and heated copper or air and phosphorus all but Fox and Winkler, believing this to be nitrogen. Fox corrected in some way to pure nitrogen but his results given on p. 73 of his paper (Faraday Society edition) do not agree with his correct formula for obtaining α_N already mentioned.

In Table II Fox's results for atmospheric nitrogen calculated to α_N by his formula are taken from Landolt and Börnstein. They differ from his published figures as will be seen; but those I have recalculated are certainly correctly reduced. Winkler's results are from the same source and Hamberg's figures have been multiplied by 0 9827.

TABLE II

One litre of distilled water absorbs from N_2 *at a pressure of 760 mm* + tension of aqueous vapour millilitres of the gas.

According to	At 0°	5°	10°	15°	20°	25°
Hamberg	23.79	21.05	18.81	17.03	15.70	14.68
Winkler (L and B)	23.12	20.50	18.29	16.56	15.18	14.10
Fox (L and B)	23.19	20.68	18.63	17.02	15.72	14.65
Fox (paper)	23.00	20.64	18.54	16.84	15.54	14.43
Braun		21.73	20.03	17.89	16.21	14.32
Adeney and Becker		20.80	18.60	17.01	15.60	14.45

I have graphically interpolated Adeney and Becker's values which it will be seen agree well with Fox's and Hamberg's. Braun's results agree with those of no other worker.

We now come to the case of greatest practical interest, that of

Atmospheric Nitrogen in Sea Water

Only four workers appear to have interested themselves in this matter and of these two, Dittmar and Tornöe left only the most casual record of the salt content of the water they used. Tornöe said he used a sea water of somewhat high density whilst Dittmar's artificial sea water was prepared" so as to represent about an average Challenger water." Hamberg, commenting on this uncertainty, informs us that he himself used waters of 1.7784%, 2.6580% and 3.5126% content of total salts whilst Fox used made up sea water containing about 7.5, 15.20 and 23 per mille Cl′. Hamberg used the following expressions

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[1] L. Braun: Z. physik Chem., **33**, 721 (1900). "Uber die Absorption von Stickstoff und von Wasserstoff in wasserigen Lösungen verschieden dissocierter Stoffe."

[2] W. E. Adeney and H. G. Becker: Proc. Roy. Dublin Soc. (2) **15**, 44, 609 (1919). "The Determination of the Rate of absorption of Atmospheric Nitrogen and Oxygen by Water."

Water of salt content	Absorbs at 760 mm dry air pressure and the temperature to form atmospheric air the quantity of nitrogen in ccs.
0.0%	$19.139 - 0.48616\ t + 0.009307\ t^2 - 0.000006353\ t^3$
1.0%	$17.712 - 0.42828\ t + 0.0078736\ t^2 - 0.000005362\ t^3$
2.0%	$16.446 - 0.38260\ t + 0.0068794\ t^2 - 0.000004698\ t^3$
3.0%	$15.342 - 0.34922\ t + 0.0063180\ t^2 - 0.000004360\ t^3$
3.5%	$14.851 - 0.33720\ t + 0.006200\ t^2 - 0.000004313\ t^3$

and gave a table for the nitrogen content of water of these salinities for each degree of temperature from $-3°$ to $+25°$. Fox used the following expression in calculating a table for atmospheric nitrogen at a dry pressure of 760 mm for each 4° from 0° to 28° and for each 4 parts of Cl′ per thousand from 0 to

$$1000\alpha = 18.639 - 0.4304\ t + 0.007453\ t^2 - 0.0000549\ t^3 - \mathrm{Cl}'\ (0.2172 - 0.007187\ t + 0.0000952\ t^2)$$

In order to compare the results of these two workers I have calculated from Knudsen's relationship—total salt content = 1.805 Cl′ + 0.03 the Cl′ content corresponding to the salt contents for which Hamberg has given values and used Fox's correcting term for Cl′ for the 4° intervals selected by this worker. The results are given in Table III.

TABLE III

Number of millilitres of atmospheric nitrogen absorbed from air at a pressure of 760 mm + tension of aqueous vapour by water of the salinity or chlorions content indicated at temperatures between 0° and 24°.

S°/₀₀	Cl′°/₀₀	0°	4°	8°	12°	16°	20°	24°
0.00	H	19.14	17.34	15.81	14.53	13.48	12.63	11.95
	F	0.00	18.64	17.02	15.63	14.45	13.45	12.59	11.86
10.00	H	17.71	16.12	14.76	13.61	12.66	11.87	11.23
	F	5.52	17.44	15.97	14.71	13.56	12.75	11.97	11.31
20.00	H	16.45	15.02	13.80	12.76	11.89	11.17	10.58
	F	11.06	16.24	14.92	13.80	12.85	12.05	11.36	10.76
30.00	H	14.34	14.04	12.93	11.99	11.19	10.54	10.00
	F	16.63	15.03	13.86	12.87	12.04	11.35	10.73	10.21
35.00	H	14.85	13.60	12.43	11.62	10.87	10.25	9.73
	F	19.37	14.43	13.34	12.42	11.65	11.00	10.43	9.93

H = Hamberg's values. S °/₀₀ = Total salts (gms) in 1000 gms.
F = Fox's values. Cl′°/₀₀ = Chlorions (gms) in 1000 gms.

It will be seen that the middle parts of the table agree well but that the two sets of figures are rather far apart at temperatures below 8° and for the higher temperatures at the higher salinities. The uncertainty as to saturation is only appreciable above 2% for distilled water and strong sea water at 0°.

On this point it may be recalled that Hamberg commenting on the difference of Tornöe's results from his says. "Für 0°, die Temperatur bei welcher die Unterschiede zwischen Tornöe's, Dittmar's und meinen Resultaten am grössten sind, is die Zahl, welche ich gefunden habe die Durchschnittzahl von neun einfachen, gut mit einander ueberstimmenden Bestimmungen." This seems to point to the probable accuracy of the higher figure.

In 1923 I published a graph[1] showing the proportions of "nitrogen" and oxygen absorbed from air at a total pressure (air + water vapours) of 760 mm and varying temperature and salinities. In using this, which is based on Fox's values regard should be had to the likelihood that values in the regions just indicated are lower than they should be.

Probable Causes of the Discrepancies between the Results of Different Observers

The differences which have been shown to exist between the results of workers who seem to have used great care are, when all corrections have been made, larger than one would be inclined to expect. I suggest the following causes as contributory.

1. The slowness of exchanges between gas and liquid phases as saturation is approached causes the differences of tension or volume of the gas phase to be so small that the human tendency to consider them insignificant may overcome sound judgment. The accuracy of an absorptionmetric experiment depends in the first place on the absolute freedom of the liquid from the gas or any gas at the beginning, that is, its tension should be exactly that of saturated water vapour, and secondly on the exact measurement of the loss of volume or tension of the gas. In a boiling-out or pumping-out experiment there seems to be no very exact criterion of the end of the exhaustion as aqueous vapour is ever present.

2. The changes in the properties of water towards the freezing point may have some effect: (a) the viscosity increases very rapidly as the water cools and the effect of agitation in mixing the liquid will no doubt be much decreased: (b) it seems probable that the region of maximum density may introduce some anomalies which a careful study would disclose.

3. The real difficulty of freezing water from air by boiling was pointed out by Leduc[2] in his work on the density of ice. He found it impossible (contrary to Bunsen's statement) to get a clear ice from water which had only been boiled and even after three freezings in vacuo under "huile de vaseline" found some cloudiness. The density of this ice was 0.0004 higher than that from boiled water. Leduc made the following

"*Remarque relative à l'analyse des gaz en dissolution dans l'eau.*

On voit, par ce qui précède, que l' eau longuement bouillie retiens une quantité de gaz fort appréciable, qu'elle abandonne au moins partiellement en se congelant. . . .

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[1] J. H. Coste: **48**, 433, (1923) "The Absorption of Atmospheric Gases by Water," Analyst.

[2] A. Leduc: Compt. rend., **142**, 149 (1906). "Sur la densité de la glace."

Il en resulte que l' analyse des gaz de l'eau, telle qu'elle se pratique toujours, est incomplète et par suite inexacte.

Si l' on admet que l'écart entre le nombre de Bunsen et le mien est dû uniquement à ce que ce savant a solidifié complètement de l'eau simplement privée de gas par ébullition prolongée on arrive à cette conclusion que cette eau renfermait encore près de 1 cm^3 de gaz par litre mésuré sous la pression atmospherique). . . ."

This observation of Leduc's shows that in the absorptiometric method there is some danger of incomplete preliminary removal of the gases of air from water. The result of this would be that less gas would be absorbed in the actual experiment than would have been absorbed by air-free water. A similar error is liable to affect the final extraction of gas in the boiling-out class of methods by reducing the actual volume of gas yielded by the water. It seems unlikely that the error should be as great as Leduc seems, on indirect evidence, to suggest.

The separation of dissolved gases from water when it freezes is one of the troubles of the maker of artificial ice. A clearer and more marketable product is obtained from gas-freed water. R. T. Gunther[1] has also called attention to the beautiful forms assumed by the chains of air bubbles which separate when water in a bottle is allowed to freeze slowly by exposure in frosty weather.

It would appear that the best way of extracting dissolved gases from water is to introduce the water into a vacuous vessel, boil, freeze evacuate, melt, boil, freeze and again evacuate, repeating the cycle until a clear ice is obtained and no more gas can be collected. The low tension of aqueous vapour at 0° (4.579 mm) would prevent the volatilisation of much water during evacuation.

I hope as the time may allow, to make some determinations of the solubility of nitrogen, using the method of congelation for freezing the water from gas.

Summary

When the proper allowances have been made for the effect of argon on the solubility of atmospheric nitrogen, considerable uncertainty exists as to the absorption coefficients of both this mixed gas and pure nitrogen in distilled water.

A similar uncertainty exists in the case of sea water.

Hamberg's and Fox's results obtained by different methods agree well in most cases. There is some reason for considering Hamberg's results more exact than Fox's at low temperatures (below 8°).

Congelation appears to be the best means of freeing water from dissolved gases.

Teddington
June, 1926.

[1] Nature, Jan. 11 (1917).

THE ADSORPTION OF GASES BY METALLIZED SILICA GELS[1]

BY L. H. REYERSON AND L. E. SWEARINGEN

The problem of specific adsorption has attracted considerable attention in recent years. The work of Langmuir and Harkins has focused attention upon molecular orientation at surfaces while the work of Taylor and his colleagues at Princeton has been correlating adsorption and catalytic activity. Considerable work has been published on specific adsorption as well as the large amount of work which has appeared on non-specific adsorptions such as adsorptions by charcoals and silica gel. The following investigation was begun with the view of studying specific adsorption by metals using silica gel as the support material and later using the information in catalytic studies.

In the case of the metallized silica gels the adsorption of gases would in general be that of silica gel itself plus any specific adsorption which might be due to the metals which has been deposited as films on the surfaces of the gel itself. This would be true provided the deposition of metal did not appreciably cut down the effective surface for adsorption on the one hand. On the other hand it is barely possible that the deposition of metals might actually increase the total surface available for adsorption. Certain experiments reported in this paper give evidence that the extension of surface plays no important role. The results indicate that specific adsorptions may be superimposed upon non specific adsorptions.

Experimental

The metallized gels used in this investigation were prepared according to the method of Latshaw and Reyerson[2]. After reduction by adsorbed hydrogen the metallized gels were dried at 110° in an atmosphere of hydrogen. In the case of the copper-treated gel it was found necessary to complete the reduction in hydrogen at higher temperatures since the first reduction seldom reduced the cupric ion below the cuprous condition. Adsorptions were measured for silica gel and silica gel metallized with silver, copper, platinum and palladium respectively. Adsorption isotherms were obtained for oxygen, carbon monoxide, carbon dioxide, methane and ethylene upon silverized gel at various temperatures. In the cases of platinized, palladized and copperized gels, the adsorption of hydrogen and sulphur dioxide was also measured. The adsorption measurements were carried out in an apparatus as shown in Fig. 1. Briefly the apparatus consisted of an adsorption bulb, A, connected by glass tubing to a mercury manometer, B, and a water-jacketed gas-measuring burette, C. This system was connected to the evacuating system by glass tubing with a stop cock at E. The gas burette was 50 cc. capacity and it was

[1] The work described in this paper formed part of a thesis submitted to the Graduated Faculty of the University of Minnesota by L. E. Swearingen in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June 1926.

[2] J. Am. Chem. Soc., **47**, 610 (1925).

graduated to tenths of cubic centimeters. Mercury was used as the confining liquid in this burette. A vacuum was produced in the system by a Stimpson double suction mercury vapor pump, supported by a Cenco Hy Vac pump. A McLeod gauge for measuring pressure was sealed directly into the glass mercury pump.

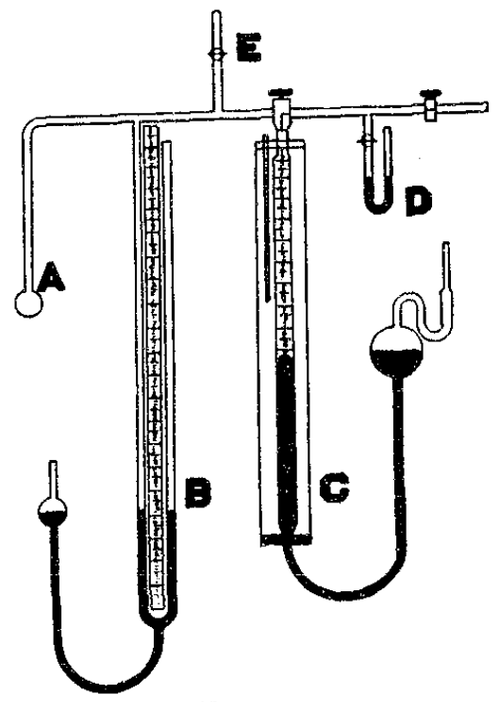


FIG. 1

The gases used in the adsorption measurements were obtained and purified in the following manner. The nitrogen used in the early part of the work was prepared by heating a solution of equal parts of sodium nitrite, ammonium sulphate and sodium dichromate. The gas was passed over heated copper turnings to remove any oxygen and then collected and stored over water. Before use the gas was dried by passing it through concentrated sulphuric acid and then through a tube containing phosphorus pentoxide. Later in the work a tank of nitrogen was obtained that analyzed 99.7% nitrogen. This gas was first passed through alkaline pyrogallol and then dried as above before use.

Carbon monoxide was prepared, as needed, by the interaction of sulphuric and formic acids. The sulphuric acid was heated, in a suitable container, on a steam bath and the formic acid was admitted by means of a separatory funnel. The gas was bubbled through a solution of potassium hydroxide and then through concentrated sulphuric acid. It was finally dried over phosphorus pentoxide before use.

The carbon dioxide was obtained from a tank of commercial gas. It was adsorbed more than 99% by a solution of potassium hydroxide. The gas was dried over sulphuric acid and then passed through a tube containing granules of anhydrous calcium chloride.

The oxygen used was taken from a tank of compressed oxygen. It was adsorbed more than 99% by an alkaline solution of pyrogallol. It was dried by bubbling twice through concentrated sulphuric acid.

The hydrogen was obtained from a tank of electrolytic hydrogen. The gas was passed through a solution of alkaline pyrogallol and then through a tube containing some platinized silica gel. This tube of gel was heated to 120° to 130°. It had been previously found that the platinized gel would cause small percentages of oxygen to combine completely with hydrogen at these temperatures. The hydrogen was finally dried over phosphorus pentoxide.

The methane used was obtained from the Carbide and Carbon Chemical Corporation and was taken as needed from a tank of the compressed gas. The gas was washed with water, passed through a solution of alkaline pyrogallol,

and then dried by bubbling twice through concentrated sulphuric acid. The ethylene was used from a tank of compressed gas which had been prepared commercially for anaesthesia. Analysis showed it to be 97% pure. It was for our purposes washed successively with water, sulphuric acid, and a solution of potassium hydroxide. It was finally dried over sulphuric acid.

The helium which was used to determine the volume of the bulb was obtained through the courtesy of the Bureau of Mines. The sample as obtained contained about 94% of helium. The principal impurity was nitrogen. The impurities were adsorbed by passing the gas through a tube of cocoanut charcoal immersed in liquid air.

The adsorption measurements were made in essentially the following manner. A sample of the gel was first weighed into the adsorption bulb, A, and the bulb sealed to the apparatus. Before making adsorption measurements the entire apparatus was washed with the gas whose adsorption was to be measured. An exception to this procedure was made in the case of carbon monoxide and the platinized gel. The preliminary washing was omitted in this case because the work of Taylor and Burns[1] had shown that the adsorption of carbon monoxide by platinum had been reduced by about 63% following an initial treatment with carbon monoxide. The bulb containing the gel sample was then immersed in an oil bath which was heated to 200°, and the evacuating pumps started. In order to obtain consistent results it was necessary to adopt a uniform proceedure. The bulb was heated at 200° for a period of three hours and the vacuum pumps were operated continuously during the entire period. During the process of evacuation the gas burette would be filled with the gas which was to be adsorbed. After remaining in the burette for about two hours, the gas volume, the temperature of the water jacket and the barometric pressure were recorded. By means of the leveling tube, D, a fine adjustment to atmospheric pressure could be obtained in determining the volume of the gas in the burette.

Upon completion of the evacuation process, stop-cock, E, was turned so that the connection to the pumps was broken. The oil bath was removed and the bulb brought to the temperature at which the adsorption was to be measured. Adsorptions were measured at the following temperatures: 0°, 64.5°, 100°, 138° and 218°. At 0° finely cracked ice mixed with water was used in a Dewar flask. Boiling methyl alcohol was used for the temperature of 64.5°, boiling water at 100°, boiling xylene at 138°, and boiling napthalene at 218°. In each case these liquids were contained in large flasks equipped with reflux condensers and in no case was the adsorption bulb permitted to come in contact with the boiling liquid, but it was bathed in the vapors from the liquid. After the adsorption bulb and contents had reached temperature equilibrium, the manometer was read and gas admitted from the gas burette through the stop-cock at the top of the burette. The gas was added in small quantities, the successive additions being made only after the manometer indicated that equilibrium had been reached. Three successive readings at

[1] J. Am. Chem. Soc., **43**, 1273 (1921).

fifteen minute intervals, which showed no change, were taken as indicating the establishment of equilibrium. The total volume of gas added, the temperature and pressure at which the added volume was measured, together with the manometer reading, were all recorded. The extent of adsorption at different pressures could readily be obtained from this data together with a knowledge of the free space in the bulb. Gas volumes were always corrected to standard conditions.

During the early part of the work, nitrogen was used to determine the free space in the bulb. The capacity of each bulb and gel sample was determined prior to the adsorption study and the adsorption of gas was taken as the difference between this volume at the several pressures and the volume of gas admitted at the given pressure, all volumes being changed to standard conditions. Later a comparison was made between the volume of a bulb as determined by nitrogen and the volume as determined by helium. In these cases silica gel was used in the bulb and two separate measurements were carried out. In one case helium was used to fill the bulb and then removed and nitrogen admitted. In the other case the gases were used in the reverse order. No difference in total volumes could be observed with the reversal of the order of admission. The comparative data for a set of measurements are given in Table I.

TABLE I

Comparative Data on the Adsorption of Helium and Nitrogen by Silica gel at 0°

Pressure in millimeters of Mercury	Volume (standard conditions) of gas admitted	Pressure in millimeters of Mercury	Volume (standard conditions) of gas admitted
Helium		Nitrogen	
40.0	1.55 cc	45.0	1.70 cc
92.0	4.00 cc	142.0	5.60 cc
160.5	6.05 cc	238.0	9.15 cc
330.0	13.00 cc	348.0	13.70 cc
540.0	20.40 cc	528.5	21.05 cc
732.8	28.10 cc	745.7	28.90 cc

If the volumes of gas are plotted against pressure it will be found that the adsorptive capacity of the gel for nitrogen and helium is essentially the same for all pressures at 0°. The maximum divergence occurs at a pressure of one atmosphere (extrapolated) and here the difference is less than 0.70 c.c. As a result of this work corrections were made to bring the value of free space to that determined by helium. The adsorption measurements in this investigation were carried out in duplicate.

Results

Table II gives a typical set of adsorption measurements and is experiment 45 in the series.

Figs. 2 and 3 show the adsorption isotherms obtained by plotting amounts adsorbed as ordinates against the pressures as abscissas. From such curves

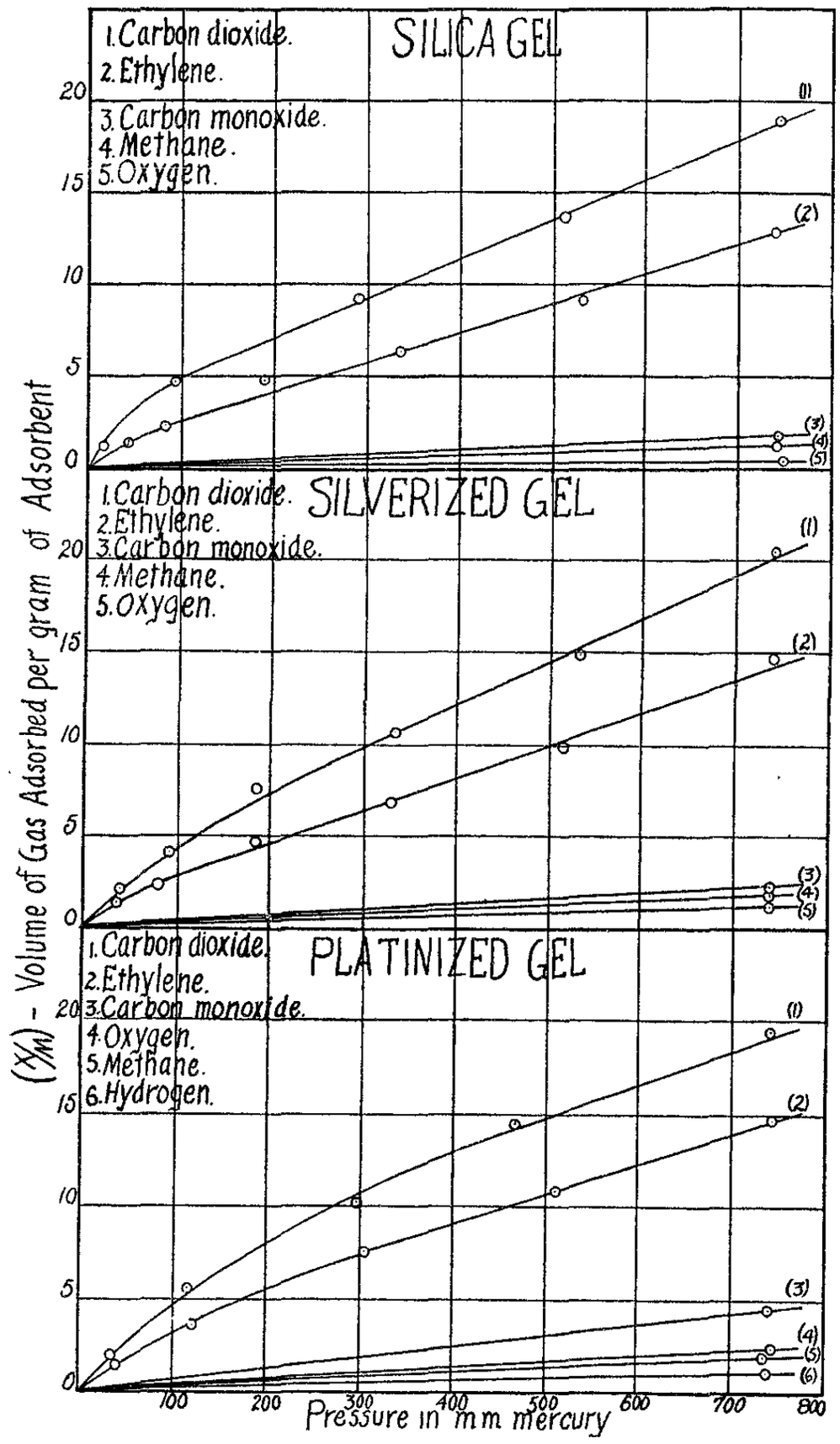


FIG. 2
Adsorption Isotherms at 0°

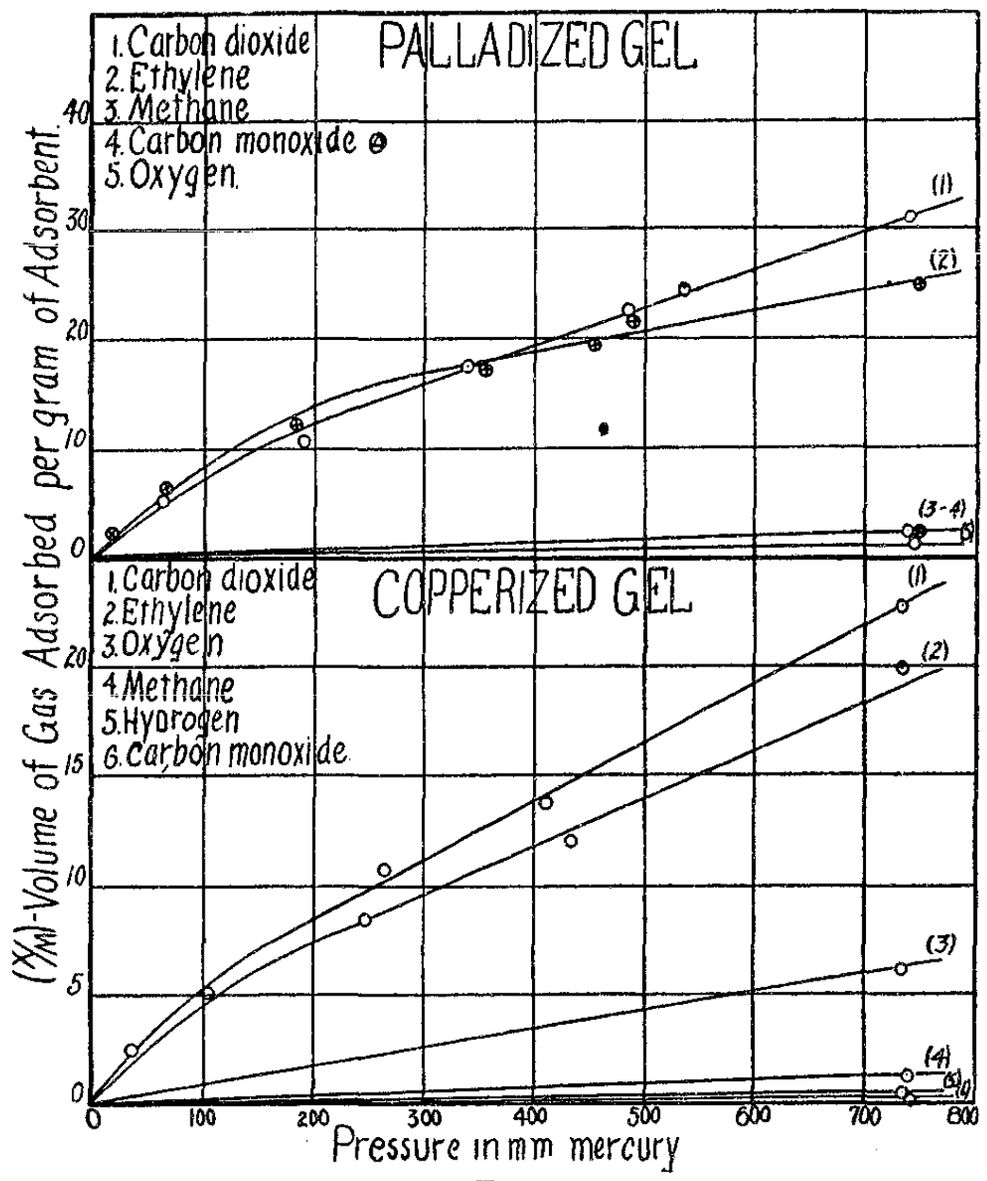


FIG. 3
Adsorption Isotherms at 0°

as these the data presented in Table III were obtained. These data give the equilibrium values at 0°. In addition to measurements at 0°, adsorptions of carbon dioxide, ethylene and sulphur dioxide were made at temperatures ranging from 0° up to 218° as indicated previously. Table IV gives the adsorption equilibrium values at actual atmospheric pressures at the time of measurement.

TABLE II

Adsorption of Ethylene by Palladized Gel at 0°

Pressure in mm. Mercury	Volume of gas admitted (cc. at standard conditions)	Free space from the helium value	X/M
20.20	3.80	.85	2.95
95.20	10.70	4.02	6.68
225.20	22.40	9.50	12.90
455.00	38.58	19.15	19.43
749.50	56.68	31.60	25.08

TABLE III

Cubic centimeters of gas adsorbed at the indicated pressures at 0°

Adsorbent	Adsorbate	Equilibrium Pressure in m.m. of Hg. 100	200	300	400	500	600	700
Silica Gel	Carbon dioxide	4.98	7.15	9.25	11.45	13.65	15.70	17.80
	Ethylene	2.51	4.20	5.80	7.45	9.00	10.60	12.25
	Carbon monoxide							1.80
	Methane							1.35
	Oxygen							0.50
	Hydrogen							0.25
Silverized Gel	Carbon dioxide	4.25	7.30	9.80	12.20	14.55	16.80	19.20
	Ethylene	2.80	4.60	6.40	8.20	10.00	11.70	13.50
	Carbon monoxide							2.30
	Methane							1.80
	Oxygen							1.20
Platinized Gel	Carbon dioxide	4.65	8.00	10.75	13.00	14.80	16.60	18.45
	Ethylene	2.60	5.50	7.40	9.20	10.65	12.40	13.95
	Carbon monoxide							4.35
	Oxygen							2.40
	Methane							1.85
	Hydrogen							1.00
Palladized Gel	Carbon dioxide	7.20	12.30	15.90	19.30	23.00	26.20	29.60
	Ethylene	8.40	14.00	17.00	18.80	20.70	22.70	24.40
	Methane							2.10
	Carbon monoxide							2.10
	Oxygen							1.00
Copperized Gel	Carbon dioxide	5.30	8.50	11.20	13.90	16.50	19.20	21.85
	Ethylene	4.50	7.45	9.60	11.85	14.00	16.15	18.40
	Oxygen							6.00
	Methane							1.40
	Hydrogen							0.60
	Carbon monoxide							0.25

TABLE IV

Effect of Temperature on Adsorptions

Pressure in m.m. Mercury	X/M c.c. adsorbed per gram of adsorbent	Temperature
Ethylene on Silica Gel		
746.50	13.62	0.00°
746.50	5.32	64.50
746.50	3.77	100.00
746.50	0.00	218.00
Carbon Dioxide on Silica Gel		
747.50	19.03	0.00°
747.50	5.66	64.50
748.50	2.56	100.00
748.00	1.78	138.00
748.00	0.00	218.00
Carbon Dioxide on Platinized Gel		
735.00	18.80	0.00°
735.00	4.38	64.50
736.00	.50	100.00
736.50	0.00	138.00
Ethylene on Platinized Gel		
739.50	14.38	0.00°
739.00	5.73	64.50
739.50	2.63	100.00
739.50	.93	138.00
Sulphur Dioxide on Platinized Gel		
739.71	100.86	0.00°
739.40	30.80	64.50
740.00	12.01	100.00
740.00	7.31	138.00
740.00	1.30	218.00

Pressure in m.m. Mercury	X/M c.c. adsorbed per gram of adsorbent	Temperature
Ethylene on Silverized Gel		
742.00	14.74	0.00°
742.70	6.69	64.50
742.70	4.56	100.00
742.70	2.86	138.00
742.80	0.00	218.00
Carbon Dioxide on Silverized Gel		
744.80	20.46	0.00°
744.00	7.46	64.50
744.00	4.32	100.00
744.00	2.86	118.00
743.90	0.00	238.00
Carbon Dioxide on Copperized Gel		
7.3300	22.75	0.00°
7.3300	6.95	64.50
7.3350	3.02	100.00
7.3340	.52	138.00
Sulphur Dioxide on Palladized Gel		
749.00	136.38	0.00°
749.00	34.73	64.50
749.20	20.80	100.00
739.20	10.00	138.00
749.40	2.64	218.00
Ethylene on Copperized Gel		
735.50	20.30	0.00°
735.00	4.65	64.50
736.00	.67	100.00
Sulphur Dioxide on Copperized Gel		
750.00	143.21	0.00°
750.00	41.65	64.50
749.00	21.20	100.00
749.00	11.70	137.00
749.00	6.20	218.00

In addition to the forgoing measurements it was thought desirable to study the effect of increasing the metal content on the adsorptive capacity of gels. Accordingly, adsorptions of carbon dioxide, carbon monoxide and ethylene were obtained upon platinized gels Nos. 1, 2, 3, and 4. Platinized

gel 1 contained the platinum from a single reduction, platinum gel 2 contained the platinum from two complete successive reductions by adsorbed hydrogen, No. 3 was subjected to three reductions and No. 4 contained the platinum from four reductions. These measurements were made at 0°. Table V gives the adsorption values for the four platinized gels.

TABLE V

ADSORPTION MEASUREMENTS ON PLATINIZED GEL 1

Pressure in m.m. Mercury	Vol. of gas admitted (c.c. N.T.P.)	Free space from the Helium value	X/M
	Ethylene		
34.00	2.70	1.31	1.39
94.00	7.20	3.63	3.57
214.00	15.20	8.25	6.95
372.00	24.80	14.35	10.45
553.00	35.68	20.60	15.08
735.70	46.17	28.40	17.77
	Carbon Dioxide		
41.50	4.00	1.60	2.40
105.50	9.60	4.07	5.53
197.50	16.50	7.63	8.87
351.45	26.50	13.55	12.95
604.50	42.75	23.35	19.40
	Carbon Monoxide		
59.90	3.10	2.30	.80
161.50	7.50	6.24	1.26
340.50	14.75	13.15	1.60
509.50	22.00	19.70	2.30
743.00	31.90	28.70	3.20

ADSORPTION MEASUREMENTS ON PLATINIZED GEL 2

	Ethylene		
32.50	2.80	1.25	1.55
82.50	6.70	3.16	3.54
206.50	14.35	7.90	6.45
394.50	25.65	15.15	10.50
752.00	44.62	28.90	15.72
	Carbon Dioxide		
37.00	2.95	1.43	1.52
111.00	7.45	4.28	3.17
194.00	13.95	7.50	6.45
374.00	25.75	14.50	11.25
684.00	44.71	26.40	18.31
	Carbon Monoxide		
45.00	2.55	1.71	.84
166.00	7.65	6.41	1.24
350.00	15.55	13.50	2.05
748.00	32.25	28.90	3.35

TABLE V Continued

Pressure in m.m. Mercury	Vol. of gas admitted (c.c. N.T.P.)	Free space from the Helium value	X/M
ADSORPTION MEASUREMENTS ON PLATINIZED GEL 3			
Ethylene			
33.50	3.60	1.29	2.31
105.00	8.65	4.06	4.59
254.00	17.80	9.80	8.00
428.00	29.35	16.50	12.85
746.40	46.55	28.80	17.75
Carbon Dioxide			
33.50	3.62	1.30	2.32
108.00	8.60	4.00	4.60
163.50	12.75	6.30	6.45
316.40	22.30	12.20	10.10
668.00	43.58	25.80	17.78
Carbon Monoxide			
50.50	2.95	1.95	1.00
159.50	7.76	6.16	1.60
301.50	13.65	11.64	2.01
489.50	22.08	18.88	3.20
733.00	32.02	28.40	3.62
ADSORPTION MEASUREMENTS ON PLATINIZED GEL 4			
Ethylene			
33.00	2.80	1.27	1.53
99.00	7.40	3.83	3.57
200.00	14.20	7.72	6.48
323.10	21.50	12.50	9.00
412.00	27.85	15.90	11.95
754.40	46.78	29.10	17.68
Carbon Dioxide			
38.00	3.90	1.45	1.45
98.00	8.20	3.76	4.44
240.50	17.60	9.24	8.36
378.00	26.08	14.50	11.58
681.00	43.48	26.15	17.33
Carbon Monoxide			
100.50	4.76	3.86	.90
240.40	11.17	9.22	1.95
428.80	18.30	16.40	2.90
745.00	32.60	28.60	4.00

Discussion of Results

To facilitate the comparison of results for the adsorption of the various gases upon the metallized gels, the adsorptions of the gases by the gels at 0° and 760 m.m. pressure has been tabulated in Table VI. The values at 760 m.m. pressure were obtained by extrapolation of the adsorption isotherms from the final equilibrium pressure which was the actual atmospheric pressure observed at the time of measurement.

TABLE VI

Comparative Data on Adsorptions by Different Gels

Gas Adsorbed	Boiling Point (Absolute temperature)	X/M for Silica Gel	X/M for Silverized Gel	X/M for Palladized Gel	X/M for Platinized Gel	X/M for Copperized Gel
H_2	20.4	0.25	——	0.00	1.10	0.55
CO	81.1	1.60	2.75	2.60	4.60	0.40
O_2	90.10	0.45	1.35	2.00	2.60	6.40
CH_4	111.4	1.75	2.20	2.40	2.05	1.40
C_2H_4	169.3	12.70	14.50	26.00	15.10	20.40
CO_2	194.6	19.40	20.70	32.00	19.60	23.00
SO_2	263.1	——	——	132.35	102.00	160.00

In the case of silica gel itself the increasing order of adsorption, with the exception of carbon monoxide, follows the increase in the boiling point. In the case of ethylene and carbon dioxide excellent adsorption isotherms were obtained. Little tendency to reach a maximum adsorption was observed in the case of these gases for the range of pressure studied. This is characteristic of nonspecific adsorptions. The adsorption of carbon dioxide is considerably higher than the values obtained by Patrick, Owens and Preston.[1] Above 200 m.m. pressure however, the two isotherms have the same ratio to each other. The difference between these values and those of Patrick, Owen and Preston can be attributed to differences in the water content of the gel and possibly the difference in granule size.

The Freundlich equation for adsorption was found to fit the data whenever there was considerable adsorption. This was also true for the adsorptions on the metallized gels. If the logarithms of the pressures are plotted as abscissas and logarthims of x/m plotted as ordinates, a straight line will result if the values fit the Freundlich equation. This is true for the data here presented.

The adsorption of the gases by the silverized gel show an increase in all cases. The order of adsorption as compared to the boiling points has not changed when compared to silica gel. Per gram of adsorbent ethylene shows the largest increase, 1.80 c.c. more of ethylene being adsorbed by the silverized gel than by the silica gel alone. On the basis of ratio increase however, oxygen and carbon monoxide are more strongly adsorbed by silverized gel than are the other gases. If we assume that the increase for carbon dioxide

[1] J. Am. Chem. Soc., **43**, 1273 (1921).

BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS
ORSAY
99

is due to change in gel structure alone, then on the basis of this ratio increase, the presence of silver in the gel has resulted in the specific adsorption of oxygen, carbon monoxide and possibly ethylene and methane.

The adsorption values for the palladized gel are not strictly comparable to the other adsorptions because the silica gel which was used was from a second preparation of the gel. It shows distinctly greater adsorptive capacity for carbon dioxide. This may be attributed largely to gel structure since Taylor and Burns[1] have shown that palladium adsorbs carbon dioxide but slightly. If we make this assumption then by comparison with the data on the first silica gel the gel containing the palladium should adsorb 2.63 c.c. of carbon monoxide, 0.74 c.c. of oxygen, 2.88 c.c. of methane and 20.90 c.c. of ethylene. We find good agreement between these calculated values and the observed results in the case of carbon monoxide and methane. Oxygen seems to be specifically adsorbed by the palladium and there is not much doubt that ethylene is very strongly adsorbed, since there is an adsorption of more than 5 c.c. above the calculated value. Specific adsorption of ethylene by the palladized gel is further indicated by the shape of the adsorption curve. More ethylene is adsorbed at low pressures than carbon dioxide while the carbon dioxide is more strongly adsorbed near atmospheric pressures. This type of curve is a characteristic of specific adsorptions.

In the case of hydrogen the first experimental work indicated zero adsorption. This might be due to two separate factors. Either the drying in an atmosphere of hydrogen filled the palladized gel with hydrogen and this was not subsequently removed by the heating and evacuation, or the palladium surface had become poisoned as regards hydrogen adsorption. Taylor and Burns[2] have shown that palladium exhibits considerable reluctance in giving up hydrogen so that the first explanation is plausible. Additional work seems to eliminate this possibility in these experiments. Pollard[3] has shown that traces of grease poison platinum as far as adsorption of hydrogen is concerned. Accordingly, additional experiments were carried out using the utmost precaution to keep grease away from the palladized gel. The palladized gel then showed an adsorptive capacity of 0.76 c.c. of hydrogen per gram of metallized gel at 0° and 760 m.m. pressure. A repetition of the adsorption measurements decreased the adsorption to 0.55 c.c. per gram of gel. A second set of experiments was then carried out. The palladized gel was first heated in an atmosphere of nitrogen at 120°-140° for a period of four hours. It was felt that this might partially remove any adsorbed hydrogen. The regular procedure for adsorption study was then carried out. The adsorption determined in this experiment gave a value of 0.87 c.c. per gram of the metallized gel. This is so close to the value previously obtained that no further work was done on this phase of the problem. It would appear from these results that palladium is also very easily poisoned as far as hydrogen adsorption is concerned. An

[1] J. Am. Chem. Soc., **29**, 421 (1925).
[2] J. Am. Chem. Soc., **43**, 1273 (1921).
[3] J. Phys. Chem., **27**, 356 (1923).

adsorption of 0.87 c.c. of hydrogen per gram of palladized gel does not indicate a marked specific adsorption of hydrogen by the palladium present in the gel.

The platinized gel was prepared upon the same silica gel as was used in all of the work except the palladized gels. It is evident from the adsorption values that there is no longer much relation between amounts adsorbed and boiling points of the substances adsorbed. The amount of carbon dioxide adsorbed is the same as for silica gel itself. The presence of platinum in the gel has considerably increased the capacity of the gel to take up ethylene. The adsorption of methane has not greatly increased. However, in the cases of hydrogen, oxygen, and carbon monoxide the platinized gel is able to adsorb from three to five times as much gas as the silica gel. The marked adsorption of carbon monoxide fits well with the experiments of Pollard and the adsorption of hydrogen, oxygen, and carbon monoxide agrees well with the work of Taylor and Burns on platinum black.

The copperized gel shows very different adsorptive capacity when compared to the other adsorbents. There is less carbon monoxide and methane adsorbed than for the unmetallized gel. Hydrogen is about twice as strongly adsorbed while large increases are noted for the other gases. About thirteen times as much oxygen is adsorbed as for the gel itself and this may even mean reaction of the copper film with oxygen. It is evident that the copper in the gel specifically adsorbs oxygen and ethylene and perhaps hydrogen, carbon dioxide and sulphur dioxide.

The effect of temperature upon the adsorption of the gases is the same as expected. Increased temperature rapidly cuts down the adsorption. It should be noted however that the gases which are specifically adsorbed are still slightly adsorbed at a higher temperature than those not specifically adsorbed.

The effect of successive metallizations by platinum does not show any great change except in the case of carbon monoxide where a steady increase in amount adsorbed is noted in going from the singly metallized gel to that metallized four times. This tends to confirm the point of view that carbon monoxide is adsorbed specifically by platinum. In the case of ethylene a lowering of the adsorptive capacity is noted for the case of the gel twice metallized and then there is a slight increase over this value for the gels metallized three and four times. Specific adsorption by the platinum may be overcoming the filling of the capillaries in the gel by the metal.

Summary

1—The adsorption of gases upon silica gels metallized with silver, copper, platinum and palladium has been measured.

2—Hydrogen is adsorbed appreciably more upon the copper, platinum and palladium treated gels.

3—Carbon monoxide is specifically adsorbed by all the metallized gels except copper.

4—Oxygen is very specifically adsorbed by the copperized gel. The other metallized gels also exhibit specific adsorption for oxygen.

5—There appears to be no marked specific adsorption of the gels for methane.

6—The metallized silica gels all adsorb ethylene more strongly than does silica gel.

7—The adsorption of carbon dioxide gives little evidence of a specific effect except perhaps in the case of copper.

The School of Chemistry,
University of Minnesota,
Minneapolis, Minnesota.

A STUDY OF THE MECHANISM OF THE CATALYTIC DECOMPOSITION OF ESTERS BY NICKEL

J. N. PEARCE AND C. N. OTT

The catalytic properties of finely divided nickel recently reduced from its oxide were first noted by Sabatier[1] about 1880. He and his co-workers, and others, have since made a great number of further discoveries of uses for nickel prepared in this way. The most important of these are met with in the hydrogenation of the unsaturated organic compounds. Nickel may also act catalytically as a dehydrogenating or as a decomposing agent under proper conditions, as in the decomposition of olefines and the aliphatic amines.

Sabatier and Mailhe[2] have shown that aliphatic acids over freshly reduced nickel break up in two ways. The first consists of the elimination of CO_2 from one molecule of acid; the second, the elimination of water and CO_2 from two molecules of acid, thus

$$(1)\quad RCOOH \longrightarrow CO_2 + RH,$$
$$(2)\quad 2\ RCOOH \longrightarrow CO_2 + H_2O + RCOR.$$

Sabatier and Senderens[3] state that ketones tend to decompose with the elimination of CO,

$$(3)\quad RCOR \longrightarrow R- + CO + -R.$$

The groups, R−, combine to some extent, but chiefly decompose to form lower hydrocarbons, hydrogen and carbon. Acetone, for example, is decomposed slowly by nickel[4] at 240°, and rapidly at 270°, yielding CO and the CH_3- radicals. The latter combine to give a little ethane; by further decomposition they yield also C_2H_4 and H_2, but the chief products formed were found to be CH_4, H_2 and C.

Nickel acts energetically on the alcohols.[3,4] Methyl alcohol begins to decompose at temperatures as low as 180°, two thirds of the aldehyde formed being destroyed. The reaction proceeds very rapidly at 250°, where eight ninths of the aldehyde is destroyed and the gaseous mixture contains forty five percent of H_2 along with CH_4 and CO. At 350° there is no longer any aldehyde and no carbon monoxide: the gas is a mixture of CH_4 and CO_2. Ethyl alcohol[3] is rapidly decomposed by nickel above 230° to give acetaldehyde and hydrogen; above 330° the aldehyde is completely decomposed into methane and CO, thus,

$$(4)\quad C_2H_5OH \longrightarrow CH_3CHO + H_2,$$
$$(5)\quad CH_3CHO \longrightarrow CH_4 + CO.$$

Similar results are obtained with propyl alcohol; seventy five percent of the aldehyde formed is decomposed at 260° by a two step process into first propyl

[1] Sabatier-Reid: "Catalysis in Organic Chemistry" (1922).
[2] Sabatier and Mailhe; Compt. rend., **152**, 1212 (1911).
[3] Sabatier and Senderens: Ann. Chim. Phys., (8), **4**, 474 (1905).
[4] Sabatier and Senderens: Ann. Chim. Phys., (8), **4**, 473 (1905).

aldehyde and hydrogen, after which the aldehyde breaks down to form C_2H_6 and CO. When alcohol vapors are passed over nickel at high temperatures we not only have the dehydrogenation to the aldehyde, but also there is possible a second side reaction which takes place with measurable velocity. In this case there is a dehydration of the alcohol to form an unsaturated hydrocarbon:

$$(6)\quad R{\cdot}CH_2CH_2OH \longrightarrow R{\cdot}CH{:}CH_2 + H_2O.$$

This reaction is inserted because it may account in part for some of the traces of unsaturated hydrocarbons found in this work.

Sabatier and Senderens[3] have found that the aldehydes are decomposed more readily than are the ketones when passed over nickel. Reduced nickel acts energetically at temperatures above 200°. Formaldehyde is decomposed to H_2 and CO. The higher aldehydes break down into CO and the next lower hydrocarbon.

Ethyl ether[1] is readily hydrogenated by nickel giving methane, a little ethane and carbon monoxide; the latter is further reduced to methane at higher temperatures. The extent of this reduction is dependent largely upon the temperature, the nature of the possible reduction products being indicated by the following reactions:

$$(7)\quad (C_2H_5)_2O + H_2 \longrightarrow C_2H_6 + C_2H_5OH,$$
$$(8)\quad C_2H_5OH \longrightarrow H_2 + CH_3CHO \longrightarrow CH_4 + CO,$$
$$(9)\quad CO + 3H_2 \longrightarrow CH_4 + H_2O.$$

Bancroft[2] states that if ether is passed over pulverulent nickel, the dissociation will probably be to $C_2H_5O + C_2H_5$, or to $C_2H_5O + C_2H_4 + H$. In the first case the final products will be $2C_2H_4$ and H_2O just as with alumina. In the second case they are likely to be $CH_3CHO + C_2H_4 + H_2$, though the ethylene and hydrogen may combine more or less completely to form ethane.

In the absence of catalysts formic esters are found to be quite stable. No appreciable decomposition is observed when ethyl formate is passed through a glass tube at 400°, but the decomposition is very rapid when the ether is in contact with catalysts that decompose formic acid. Furthermore, the decomposition takes place at temperatures which are lower than those required for the esters of other aliphatic acids, but higher than those required for formic acid. Sabatier and Mailhe[3] have shown that this decomposition takes place according to two different reactions at the same time, the one similar to the usual decomposition of esters of other aliphatic acids:

$$(10)\quad 2\ HCO_2C_nH_{2n+1} \longrightarrow HCOH + CO_2 + (C_nH_{2n+1})_2O,$$
$$(11)\quad HCO_2C_nH_{2n+1} \longrightarrow CO + C_nH_{2n+1}OH.$$

The whole or part of the alcohol formed is dissociated at the reaction temperature into hydrogen and aldehyde, the aldehyde in turn being unstable dissociates into CO and a hydrocarbon. Formic esters are easily decomposed by nickel above 220°.

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[1] Sabatier and Senderens: Bull., (3) **33**, 616 (1905).
[2] Bancroft: "Catalysis in Organic Chemistry," by Sabatier and Reid, 18cm.
[3] Sabatier and Mailhe: Compt. rend., **154**, 49 (1912).

The direct hydrogenation of carbon monoxide over nickel[1] begins at around 180°-200° and goes on rapidly without complications at 230°-250°. With the theoretical mixture of hydrogen and carbon monoxide, 3:1, the reaction is practically complete, the resulting gas being nearly pure methane. The reaction is always less complete when the carbon monoxide is in excess. If the operation is carried out at temperatures above 230° complications arise due to the decarbonization of the carbon monoxide which is accelerated by the nickel.

$$(12) \quad 2\,CO \longrightarrow C + CO_2.$$

The decomposition increases with rise in temperature and is complete at 350°, if the flow of gas over the catalyst is sufficiently slow. The carbon dioxide which is thus formed is partially hydrogenated. Its proportion is greater, the higher the temperature, since the secondary reaction which produces it is greatly accelerated by rise of temperature. Thus, when operating at 380° with the theoretical mixture which gives methane completely at 250°, a gas is obtained which contains by volume: CO_2, 10%, CH_4, 67.9%, H_2, 21.6%. When the percentage of carbon monoxide is sufficiently increased, the hydrogenation is greatly weakened; much hydrogen passes through and the proportion of carbon dioxide becomes very large.[2]

Like carbon monoxide, carbon dioxide is readily hydrogenated over nickel to form methane:

$$(13) \quad CO_2 + 4H_2 = CH_4 + 2H_2O.$$

The reaction begins at a higher temperature than with carbon monoxide, about 230°, and is rapid above 300°. With sufficient excess of hydrogen the carbon dioxide disappears almost completely.

Theoretically the decomposition of esters by nickel might take place in one or more of several different ways. Ethyl acetate, for example, might decompose to form the CH_3- and the $-COOC_2H_5$ radicals which in the presence of hydrogen should form, respectively, methane and ethyl formate, or the ultimate reduction products of the latter, namely, methane and carbon monoxide:

$$\text{(I)} \quad CH_2COOC_2H_5 \longrightarrow CH_3- + -COOC_2H_5,$$
$$CH_3COOC_2H_5 + H_2 \longrightarrow CH_4 + HCOOC_2H_5,$$
$$HCOOC_2H_5 \longrightarrow CO + C_2H_5OH \longrightarrow CH_4 + CO + H_2.$$

The ester might break down to form the ethyl and acetate radicals, which with hydrogen would give ethane and acetic acid, or its decomposition products:

$$\text{(II)} \quad CH_3COOC_2H_5 \longrightarrow CH_3COO- + -C_2H_5,$$
$$CH_3COOC_2H_5 + H_2 \longrightarrow C_2H_6 + CH_3COOH \longrightarrow CH_4 + CO_2.$$

Further, the ester might decompose more completely to form carbon dioxide, the methyl and ethyl radicals, or possibly carbon dioxide and some propane. In the former case we should expect to obtain methane, ethane and perhaps the reduction products of carbon dioxide, if hydrogen were present.

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[1] Sabatier and Senderens: Bull., (3) **29**, 294 (1908).

[2] Sabatier and Senderens: Compt. rend., **134**, 514 (1902).

(III) $CH_3COOC_2H_5 \longrightarrow CO_2 + CH_3^- + -C_2H_5$, or $CO_2 + C_3H_8$,
$CH_3COOC_2H_5 + H_2 \longrightarrow CO_2 + CH_4 + C_2H_6$.

Finally, as in the case of the aliphatic acids, it is possible for two molecules of the ester to decompose simultaneously into carbon dioxide, acetone and ethyl ether, thus,

(IV) $2(CH_3COOC_2H_5) \longrightarrow (CH_3)_2CO + (C_2H_5)_2O + CO_2$.

As previously mentioned,[2] the acetone may then break down to give methane, carbon monoxide, hydrogen, carbon, and some ethane and ethylene, while the ether[5] in the presence of hydrogen would be reduced to methane, ethane and carbon monoxide. As is evident, it is possible to apply similarly the various decomposition schemes just mentioned to other esters.

Bancroft[1] states that when ethyl acetate is decomposed by being passed over nickel, carbon dioxide and propane are formed. He says that the reaction is probably not complete, but does not state at what temperature this decomposition takes place. He further points out the lack of knowledge of the exact mechanism of the reaction, and suggests that hydrogen be mixed with the ester before it is passed over the nickel so that the decomposition products may be reduced before they have opportunity to react with each other, and may thus be identified.

A study, therefore, of the products formed when an ester is passed over nickel, both in the presence and in the absence of added hydrogen, should throw some light on the mechanism of its decomposition. In a previous paper Pearce and Ott[2] studied the decomposition of ethyl acetate by nickel at temperatures between 300° and 450°. From the nature of the products obtained they concluded that the initial decomposition is most probably represented by scheme (IV): $2\ CH_3CO_2C_2H_5 \longrightarrow (CH_3)_2CO + (C_2H_5)_2O + CO_2$. The acetone and ether formed were then decomposed to products stable at the temperatures involved. The decomposition products which were actually found are identically the same as those demanded by such a step-wise scheme of decomposition. They also found that the addition of gaseous hydrogen to the ester vapor before passing over the catalyst causes no change in the nature of the products formed. This might have been expected since hydrogen is actually formed in the reaction. It was also found that raising the temperature increases the amount of carbon dioxide and methane in the products, and decreases the amounts of carbon monoxide and hydrogen, probably due to facilitation of the secondary reactions:

$$2CO \longrightarrow CO_2 + C, \text{ and}$$
$$CO + 2H_2 \longrightarrow CH + 2H_2O.$$

In the present work we have extended the study to the decomposition products of methyl and propyl acetates and methyl propionate at various temperatures between 300° and 700°. By this means we hoped to test further the above schemes of decomposition and to determine the effect of different groups upon it.

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[1] Sabatier and Reid: "Catalysis in Organic Chemistry," 180n (1922).
[2] Pearce and Ott: J. Phys. Chem., **28**, 1201 (1924).

Materials used

ESTERS. The original samples were washed several times with distilled water, a saturated salt solution being used in the case of methyl acetate. An equal volume of water was then added and the ester distilled off. The distillate was dried over anhydrous potassium carbonate for several days, then over phosphorus pentoxide, and finally fractionated. The following fractions were retained: methyl acetate, 53.2°-53.4° at 745 mm.; ethyl acetate, 76.4°-76.6° at 748 mm.; propyl acetate, 101°-102° at 747 mm.; methyl propionate, 79°-80° at 748 mm.

NICKEL. Approximately equal parts by weight of recrystallized nickel nitrate and coarse pumice, "pea crystal," were heated together in a furnace at 400°-450° for about six hours, or until the evolution of fumes had ceased. The material was allowed to cool and was stored in a desiccator until needed. It was later reduced at the lowest possible temperature in the tube in which it was to be used. When first prepared the nickel is black in color, but after use for some time it becomes brown or gray and is only slowly soluble in dilute hydrochloric acid.

HYDROGEN. The hydrogen was generated by the electrolysis of a concentrated solution of sodium hydroxide. The gas was bubbled through sulphuric acid, then over heated copper gauze and solid sodium hydroxide.

Apparatus

The ester was placed in a 10 c.c. reservoir from which it was forced by pressure through a fine capillary into a vaporizing chamber kept at about 20° above the boiling point of the ester. The vapors passed directly into the catalyst tube which was of pyrex glass, 90 cm. long and 10 mm. internal diameter. The tube was placed in a 75 cm. electric furnace which could be used for temperatures up to 800°. The temperature of the gases was taken just as they left the catalyst by means of a calibrated copper-constantan thermocouple and are accurate to ±1.00°. The liquid portion of the products was condensed in an ice bath and the gases were collected over dilute sulphuric acid which had been previously saturated with the gases.

The gases were analyzed by means of a modified Orsat apparatus. The carbon dioxide was determined by absorption in a concentrated potassium hydroxide solution, unsaturated hydrocarbons by concentrated sulphuric acid, oxygen by alkaline pyrogallate, and carbon monoxide by acid cuprous chloride. The hydrogen and hydrocarbons were determined by fractional combustion over heated copper oxide in a quartz tube, according to the method prescribed by White.[1] The gas burette was water-jacketed and was fitted with a manometer and a pressure compensating tube.

Experimental Method

The tube of nickel oxide was placed in the furnace and the heat and hydrogen turned on, thus allowing the reduction to take place at the lowest possible temperature. After five or six hours, when the furnace had reached the de-

[1] White: "Technical Gas and Fuel Analysis," 54 (1913).

sired temperature and the nickel was fully reduced, as evidenced by no further formation of water vapor, the hydrogen was shut off and the vapor of the ester was admitted. In all cases the vapor of the ester was allowed to flow through the catalyst for at least an hour in order that all of the residual hydrogen might be displaced before the samples of the effluent gases were taken for analysis. The products were led through an ice trap where the liquefiable portion was condensed. The gaseous products were collected over dilute sulphuric acid and later analyzed. When it was desired to test the effect of added hydrogen on the decomposition products, the hydrogen was led into the vaporizing chamber where it mixed with the ester vapor before passing over the nickel, and samples of the decomposition products were taken and analyzed as before. The decomposition products from each ester were studied at several different temperatures from 300° up to 700° where sintering of the catalyst probably begins.[1] The experiments at each temperature were checked with new samples of the catalyst. In some instances second runs were made with the same catalyst to determine the influence of the age of the catalyst on the nature and the amounts of the decomposition products.

Analysis of Products

The liquid which was condensed in the ice trap at 0° was analyzed in two ways. Several different samples were fractionated through a 10-inch distilling column and in no case did the corrected boiling points differ by more than 0.2° from that of the original ester. Several samples collected at each temperature were quickly titrated at 0° with N/20 normal sodium hydroxide; these showed no measurable quantity of free acid. The purity of the condensed ester was further confirmed by density determinations at 25°.

After the removal of the carbon dioxide, unsaturated hydrocarbons and carbon monoxide, the remainder of the gas was passed over copper oxide at 240°. The contraction following this combustion is equivalent to the volume of the hydrogen in the gas mixture, since the change in the volume of the copper oxide and the volume of the liquid water formed are negligible; the contraction from the subsequent passage of the residue over potassium hydroxide solution would be due to hydrocarbons higher than propane, but none were even found. The remaining gases were passed over copper oxide at 300°. At this temperature propane is burned, and one-half of the increase in volume following this combustion should be considered equal to the volume of propane. To determine the ethane present the residual gases were next passed over copper oxide at 380°, or above; the increase in volume following this combustion is equal to the volume of ethane originally present. The remainder of the gas was considered as methane which burns over copper oxide only when heated to redness. No attempt was made to determine the amount of water vapor formed during the decomposition of the esters; it was condensed along with the undecomposed ester in the trap at 0°.

[1] Smith: J. Chem. Soc., **123**, 2088 (1923).

Experimental Results

The experimental results are recorded in Tables I-IV. The experimental temperatures are given in the top horizontal row; the vertical columns contain the percentages of the constituents indicated at the left. The first four columns in each table are obtained from the analysis of the decomposition products of the ester alone. The fifth column shows the effect of the previous addition of hydrogen to the ester before passing it over the catalyst. In the sixth column, when given, are collected the corresponding data obtained by means of a sample of catalyst which had been used for some time previously at the same temperature. Each value given is the mean of at least two independent determinations, differing usually by not more than one percent.

TABLE I
Gaseous Products from the Catalytic Decomposition of Methyl Acetate by Nickel

Temp.	365°	469°	560°	662°	470° ($+H_2$)
CO_2	3.0	12.8	12.3	15.5	7.6
CO	26.0	25.9	27.5	19.4	18.9
H_2	61.5	35.3	21.7	20.0	48.2
CH_4	4.0	30.3	35.4	43.5	22.8
C_2H_6	5.7	4.7	trace	trace	none
Unsat'd	trace	trace	trace	none	none

TABLE II
Gaseous Products from the Catalytic Decomposition of Propyl Acetate by Nickel

Temp.	374°	470°	572°	725°	570° ($+H_2$)	374° (old)
CO_2	6.7	7.0	10.0	13.4	4.8	4.0
CO	25.8	25.5	11.1	8.5	5.3	28.2
H_2	32.8	29.8	28.8	26.2	65.4	35.6
CH_4	19.8	23.1	44.0	47.8	21.8	16.1
C_2H_6	12.2	10.3	5.3	2.8	2.4	12.7
Unsat'd	2.3	3.1	trace	none	none	3.3

TABLE III
Gaseous Products from the Catalytic Decomposition of Ethyl Acetate by Nickel

Temp.	300°	350°	400°	450°	400° ($+H_2$)	400° (old)
CO_2	10.0	9.2	18.0	19.4	8.8	8.4
CO	22.9	24.0	19.9	18.2	9.4	28.8
H_2	33.4	34.8	18.7	14.2	54.9	22.6
CH_4	30.3	32.4	43.7	46.8	26.7	40.0
C_2H_6	3.0	trace	none	1.2(?)	none	none
Unsat'd	0.6	trace	trace	none	none	none

TABLE IV

Gasseous Products from the Catalytic Decomposition of Methyl Propionate by Nickel

Temp.	420°	468°	560°	668°	470° ($+H_2$)
CO_2	15.8	16.3	16.0	14.9	7.1
CO	13.7	16.6	10.0	6.6	6.9
H_2	31.4	25.7	20.6	18.1	73.4
CH_4	20.0	21.9	43.0	59.2	7.1
C_2H_6	15.0	16.6	9.2	trace	5.2
C_3H_8	trace	trace	none	none	none
Unsat'd	1.0	0.7	0.7	trace	none

At a few temperatures the volume proportions of the gaseous products fail to approximate 100 by as much as two or three percent. These deviations are not considered important since we are chiefly concerned with the relative proportions of the gases in the mixture.

A comparison of the data obtained for the four esters gives a really dependable basis for deciding upon the mechanism of the decomposition of esters by nickel. It has shown also that the conclusions drawn in the previous paper[1] do not fully represent the exact mode of decomposition. It is obvious that the ester molecule will be weaker at certain points than at others. It is at the weakest point, therefore, that the rupture of the molecule will first occur and in greatest measure when it is subjected to an elevation of temperature. This does not exclude the possible occurrence of other modes of decomposition at the same time, but these will occur in lesser and different degrees depending upon the conditions of stress imposed by the temperature.

The discussion which follows is based upon the single assumption that the initial break in the molecule will occur at the weakest point, and that this point is the same for all esters of the type studied. Again let us consider ethyl acetate as our model. If it decomposes according to Scheme I, methane and ethyl formate, or the decomposition products of the latter, should be formed in the presence of hydrogen. If it breaks up according to II, the hydrogen should cause the formation of ethane and acetic acid. The latter on decomposing should give methane and carbon dioxide. If (III) is the proper scheme, the ester alone should form carbon dioxide and propane; in the presence of hydrogen there should be formed methane, ethane and carbon dioxide. It will be noted that these three schemes call for a change in the nature of the decomposition products in the presence of hydrogen. According to (IV) the ester alone should give acetone, ether and carbon dioxide, the ultimate products being carbon monoxide, carbon dioxide, hydrogen, methane, and small amounts of ethane, ethylene and carbon. Since free hydrogen is already present in the products, the addition of more molecular hydrogen should not greatly alter either the nature or the proportions of the products.

[1] Pearce and Ott: J. Phys. Chem., **28**, 1201 (1924).

Only in scheme (IV) does hydrogen appear, and then only as the product of a secondary reaction, yet even at the lower temperatures hydrogen is present in greater proportion than are any of the other gaseous products. If we consider the products formed when alcohols, aldehydes, ethers, ketones, etc., are passed over nickel, we find that hydrogen is formed only in the dehydrogenation of alcohols, the second product being the aldehyde. Formaldehyde is the exception in that it decomposes at the temperature of the reaction completely into hydrogen and carbon monoxide. There is a second source of hydrogen, namely, that formed in the decomposition of the nascent CH_3-radical, but the amount produced in this way must be small since the other products resulting from this decomposition, carbon and ethylene, are formed only in negligible quantity.

There is sufficient experimental evidence to show that, in the decomposition of esters by nickel, methane may be formed in at least three ways. Methane is formed by the direct combination of hydrogen with the CH_3-radical set free at the instant when the ester decomposes thus,

$$CH_3CO_2C_2H_5 \longrightarrow CH_3- + -CO_2C_2H_5.$$

The second product is ethyl formate. It is also formed in the decomposition of ethyl aldehyde (5), and, finally, it is produced by the complete reduction of the two oxides of carbon. A fourth source will be mentioned later.

A study of the reactions show three possible sources of carbon monoxide. They are the decomposition of aldehydes to give carbon monoxide and a hydrocarbon; the decomposition of a formate giving carbon monoxide and an alcohol, which in turn breaks up to form more carbon monoxide and a hydrocarbon; and the decomposition of acetone, yielding carbon monoxide and the two radicals, CH_3-. The last of these must be excluded for reasons which will be explained shortly.

Carbon dioxide has purposely been left to the last because it appears to be the key to the solution of the problem of the mechanism of ester decomposition. Carbon dioxide can form only as a result of the decomposition of carbon monoxide (12), from the decomposition of two moles of acid, (10) and (11), or from the primary decomposition of two moles of ester (IV). In either of the last two cases the amount of carbon dioxide formed should be equivalent to one-half of the number of moles of the acid or ester decomposed. If, on the other hand, one mole of acid decomposes according to (1), or one mole of ester according to (III), then the amount of carbon dioxide formed should be equivalent to the acid or ester decomposed. Whether the carbon dioxide comes from the acid or the ester the quantity should be large. We actually find, however, at the lowest temperatures that the volume of carbon dioxide is relatively small, and that carbon monoxide, which is not even indicated in the initial reaction schemes, is present in relatively large proportions. The fact that for the temperature range studied the percentage of carbon dioxide increases, while that of carbon monoxide decreases with rise in temperature can only lead to one conclusion, namely, that at some low temperature only carbon monoxide is formed. On the basis of these considerations for carbon

dioxide we can, therefore, exclude the possibility of the initial decomposition being represented by schemes (II), (III) and (IV).

There remains then just one plausible guess as to where the molecule first breaks when the ester is passed over nickel. It is that represented by scheme (I). Let us first consider in a general way the decomposition of the esters of acetic acid. The first original splitting common to the molecules of all such esters can be represented by the general reaction:

$$CH_3CO_2C_nH_{2n+1} \longrightarrow CH_3 + -CO_2C_nH_{2n+1}.$$

This is followed immediately by a second reaction in which these radicals are reduced to methane and the formic ester,

$$CH_3- + -CO_2C_nH_{2n+1} + 2H \longrightarrow CH_4 + HCO_2C_nH_{2n+1}.$$

Some of the methyl radicals may also combine to form ethane as will be discussed later. The formate at the temperature of the reaction decomposes to form carbon monoxide and an alcohol:

$$HCO_2C_nH_{2n+1} \longrightarrow CO + C_nH_{2n+1}OH.$$

The alcohol in turn decomposes to give hydrogen and the corresponding aldehyde:

$$C_nH_{2n+1}OH \longrightarrow 2H + C_nH_{2n}O \text{ (aldehyde)}.$$

The final step in the decomposition consists in the breaking down of the aldehyde molecule to form the next lower hydrocarbon and carbon monoxide.

It is obvious that these successive reactions cannot proceed without the presence of at least an initial trace of hydrogen. Once molecules of the alcohols have been formed, the nascent hydrogen resulting from their decomposition is sufficient to reduce all nascent CH_3- and $-CO_2R$ radicals which are subsequently formed. It should be noted at this point also that while one hydrogen atom is required to reduce a $-CO_2R$ radical to the formic ester, the alcohol resulting from this produces on decomposition two hydrogen atoms. Thus, the amount of free hydrogen in the gas mixture increases as the total reaction proceeds. Naturally, the question as to the source of the hydrogen necessary to reduce the first CH_3- and $-CO_2R$ radicals formed now arises. The stability of the individual paraffin hydrocarbons toward heat varies with their position in the homologous series. It is a well known fact that the higher hydrocarbons will on heating, and especially in the presence of a catalyst, "crack" to form simpler hydrocarbons. The stability of the paraffins increases as the complexity of the molecule becomes less. This is also exactly the order of their ease of oxidation by copper oxide.[1] Methane splits up for the most part into its elements on being led through a red-hot tube, and there is formed at the same time ethane, ethylene, acetylene, and some aromatic compounds, the proportions depending on the temperature. Ethane, ethylene and acetylene behave similarly. In the presence of the proper catalyst this kind of decomposition should take place at a much lower temperature. The free nascent CH_3- radicals are likewise unstable. Two of them

[1] White: "Technical Gas and Fuel Analysis," 54 (1913).

may combine to form an ethane molecule, but some will decompose completely to form free hydrogen and carbon, or partially to form hydrogen and unsaturated molecules. The hydrogen thus formed from the free CH_3- radicals is most probably that which reduces the radicals formed when the first ester molecules split. The fact that we obtain only traces of free carbon, and at most temperatures either none or only traces of unsaturated hydrocarbons indicates that relatively few of the methyl radicals are thus decomposed. They have either combined with each other to form ethane, or with hydrogen to form methane. Since at a given temperature methane is more stable than ethane, we should expect the tendency to form methane in the presence of hydrogen, $(CH_3 + H) \longrightarrow CH_4$), will be greater than the tendency to form ethane, $(CH_3 + CH_3) \longrightarrow C_2H_6$. This is especially true for ethyl acetate at 300°. Bancroft[1] states that heated nickel decomposes ethyl acetate to carbon dioxide and propane, but he gives no reference for the statement. We have found no evidence of propane formation.

Except in the case of propyl acetate, ethylene or other unsaturated hydrocarbons, appear only in minute quantity and then only at the lower temperatures. This would indicate that the unsaturated compounds are not formed at all, or that they are completely hydrogenated by the nickel to methane and ethane. At the higher temperatures they are not stable.

Ethyl propionate is the only ester of an acid higher than acetic acid studied. If the first split of the ester molecule is represented by, $C_2H_5CO_2CH_3 \longrightarrow C_2H_5 + -CO_2CH_3$, we might expect some butane to be formed, but none was found. Ethane should be more stable than butane at any temperature, and with hydrogen present we should expect, therefore, the formation of a considerable amount of ethane even at the lowest temperature employed, namely, 420°. Since ethane,[2] and very probably also the C_2H_5- radical, decomposes slowly above 325° to give carbon, methane, and free hydrogen, the actual amount of ethane formed will be somewhat less than the reaction equation demands; the amount of ethane produced should and does, decrease with rise in temperature. These deductions are fully confirmed by the experimental data.

Let us now turn to the consideration of the decomposition of the formic esters which are formed when the ester molecule first decomposes. The methyl formate decomposes successively according to the following reactions:

$$HCO_2CH_3 \longrightarrow CO + CH_3OH,$$
$$CH_3OH \longrightarrow H_2 + HCOH,$$
$$HCOH \longrightarrow H_2 + CO.$$

It is evident, therefore, that the complete decomposition of methyl acetate should give relatively small amounts of methane and ethane, and relatively large amounts of free hydrogen and carbon monoxide. Moreover, if the decomposition temperature is sufficiently low, no carbon dioxide should be formed. With rise in temperature carbon monoxide disappears in the formation of carbon dioxide; it is also reduced by hydrogen to form methane and

[1] Sabatier-Reid: "Catalysis in Organic Chemistry," 180 (1922).
[2] Sabatier-Reid: "Catalysis in Organic Chemistry," 911 (1922).

water. The maximum amount of carbon dioxide is never obtainable at any temperature, because it also is capable of reduction by the free hydrogen present.

Similar successive reactions could be written expressing the decomposition of the ethyl and propyl formates produced in the initial decomposition of the ethyl and propyl acetates. In each case the corresponding alcohol is first obtained. The ethyl alcohol is dehydrogenated to the aldehyde and free hydrogen. The acetaldehyde in turn yields carbon monoxide and methane. This methane together with that formed in the initial splitting of the ester molecule accounts for the large proportion of methane from ethyl acetate. From propyl acetate we should obtain ultimately ethane, hydrogen and carbon monoxide. Propyl acetate should give, therefore, and actually does give, a larger proportion of ethane than do any of the other acetic esters. Since hydrocarbons are formed from all aldehydes, except formaldehyde, the proportion of hydrogen in the effluent gases should be less than that from methyl acetate. The number of equivalents of carbon monoxide possible should be the same for all esters, if none of it is subsequently removed.

Again, we may state that no propane formation has been observed. According to the above considerations we should expect to obtain n-propane in quantity only when we decompose n-butyl acetate; n-butane from n-amyl acetate, and so on.

With none of the esters does the previous addition of hydrogen to the ester vapor appear to cause any change in the mechanism of the decomposition or in the nature of the products formed. That this is true is indicated by th fact that for each ester the ratio of the percentages of each product formed when hydrogen is initially absent to that formed when hydrogen is previously added is approximately a constant. This seems to be conclusive proof that the added hydrogen acts merely as a diluent.

A comparison of the data in the columns designated, (old), with similar data for the same temperature shows the effect of continued use of the catalyst on the decomposition products of the esters. This effect was investigated because it was observed early in the work that the proportions of the products obtained varied greatly with the age of the catalyst. The samples of the catalyst from which the recorded data were obtained had been previously used for about four hours at the given temperature. These samples were first washed with pure hydrogen for several hours at the same temperature. Finally, the ester vapor was again passed over the catalyst and the products were collected and analyzed as before. The percentages of carbon dioxide and methane in the gaseous mixture are less, while those of carbon monoxide and hydrogen are greater than in the mixtures obtained with a freshly prepared catalyst. The fact that these changes in the composition of the resulting products obtained from successive experiments with the same sample of catalyst are so marked is sufficient evidence of a rapid change in the nature and the activity of the nickel. This change in activity may be due in part to the well known poisoning effect of carbon monoxide. The change may also be

due to the deposition of other decomposition products on the surface of the nickel. That this may be true is evidenced by the fact that there is always deposited at the end of the tube a dark brown tarry film of unknown composition. Further, the nickel assumes a grayish color and dissolves in dilute hydrochloric acid much more slowly than does freshly prepared nickel.

At the lowest temperature indicated for each ester the percent of ester vapor decomposed is small, usually less than 10 percent of the ester used; the amount decomposed increased to 80 percent and above at the higher temperatures. The temperatures at which the various esters begin to decompose were found to be approximately as follows: methyl acetate, 310°; ethyl acetate, 280°; propyl acetate, 330°; methyl propionate, 360°.

Summary

The products of the catalytic decomposition of methyl, ethyl and propyl acetates, and of methyl propionate by finely divided nickel have been studied at various temperatures between 300° and 725°.

The approximate temperatures at which the different esters begin to decompose have been determined.

For all the esters studied the proportions of carbon dioxide and methane in the decomposition products were found to increase with rise in temperature; those of hydrogen and carbon monoxide decrease under the same conditions. Only traces of hydrocarbons higher than ethane were ever found. No free acid or other liquid decomposition products appeared at any temperature.

The addition of hydrogen to the vapors before passing over the nickel produces no change in the nature of the decomposition products, indicating that the mechanism of the reaction is the same with or without added hydrogen. Hydrogen is formed in the decomposition.

The activity of the catalyst is altered by some of the products resulting from the decomposition of the ester.

A scheme representing the catalytic decomposition of esters by nickel has been suggested.

Physical Chemical Laboratory,
The State University of Iowa.

-18

THE DECAY OF PHOSPHORESCENCE OF ZINC SULPHIDE

BY H. AUSTIN TAYLOR[1]

The uncertainty attached to a study of phosphorescent phenomena, despite the large amount of work already accomplished is multiplied by the diversity of opinion on what would seem to be the very fundamentals. The question, for example, as to whether some exciting element present as impurity in the phosphorescent material is a necessity for phosphorescence does not seem, even at the present time, to have been satisfactorily settled. There is evidence on this point from both directions. Again, the question of the cause and rate of decay of phosphorescence has no thoroughly satisfactory answer and both theory and practice have supporters whose ideas are mutually contradictory and conflicting. The cause of such a situation would appear to lie in the fact that the experimental work so far performed has not in many cases been of the highest order and the results obtained generalised to too great an extent, thereby involving error.

The complexity of the problem of phosphorescence then, necessitates an attack on a small portion of the phenomena first, and it is proposed herein to study the effect of temperature on the rate of decay of phosphorescence using zinc sulphide as the phosphorescent material.

The similarity between this effect and that of red and infra-red radiation suggests at once that a similar explanation holds for both. Such a suggestion has already been made by Perrin[2] and experimental evidence quoted in its favor, the whole being taken as evidence in favor of the simple radiation theory of chemical reaction. The doubt recently cast on this theory from numerous points of view necessitates a critical examination of the evidence from phosphorescence.

According to Perrin, phosphorescence is due to the emission of radiation by the phosphorogen returning to the normal state from the modified or excited state into which it was thrown by absorption of the exciting radiation. That the frequency of the phosphorescent radiation is in general lower than that of the exciting light[3] is explained by the assumption that the return from the excited to the normal state is a process occurring in numerous stages, each accompanied by its own emission and therefore of a lower order than the excitation which presumably occurs in one step. The cause of the return of the excited molecule to the normal state is to be found in the internal radiation present in the system in virtue of its temperature. If the temperature of the system is raised, the rate of return is increased, that is, the phosphorescence is increased. Alternatively if we increase the internal radiation

[1] Contribution from the Havemeyer Chemical Laboratory, New York University.

[2] Trans. Faraday Soc., **17**, 566 (1922).

[3] Stokes' Law.

of the system photochemically, as opposed to thermally, we shall again increase the rate of return of the excited molecule to its normal state, again increasing the phosphorescence.

Qualitatively the explanation appears to agree with the observed facts. Perrin however proceeds to make the theory quantitative. The regeneration of the normal phosphorogen is considered as a unimolecular chemical reaction and its rate thus measurable at different temperatures. From the temperature coefficient of this rate of decay of phosphorescence the energy of excitation,—the critical increment,—may be calculated in the usual manner and hence the frequency of radiation which should cause the more rapid decay. Perrin writes: "I have done this recently in the case of phosphorescent zinc sulphide containing copper. Measuring the increase in the brightness produced by a known rise of temperature I have succeeded in calculating the wave length, approximately 1μ of the regenerating radiation. It remains to be seen whether this infra-red radiation really regenerates the phosphorogen. . . . The spot hit by these rays of wave length 0.7 to 1.5μ emits a bright phosphorescence and very soon afterwards that spot turns dark and is then easily distinguished again from the faintly luminous background." The evidence seems unequivocal.

When we analyse the data recorded before that of Perrin however, we are immediately struck by some apparent anomalies if the theory suggested is the correct one. The experiments of Becquerel more than fifty years ago showed definitely that the radiation causing the more rapid decay of phosphorescence was not confined to a single frequency nor even a narrow band of frequencies such as the radiation theory would demand, but was general throughout the red and infra-red regions of the spectrum. More quantitative experiments of Nichols and Merritt[1] on the decay of zinc sulphide phosphorescence at different temperatures showed that the effect of temperature over large ranges is a complex effect and not at all in agreement with the unimolecularity assumed by Perrin. It was found then, that the rate of decay—temperature curve showed various maxima, one at some temperature above 20°C, another, very pronounced, at −40°C and a third at −160°C. The existence of such maxima necessarily means that the temperature coefficient of decay is negative for certain ranges; a fact hardly capable of reconciliation with Perrin's view. That such behavior could be explained on the basis of complexity of phosphorescence bands does not seem possible in view of the work of Pierce[2] in the same year, wherein he finds no change in the phosphorescent band position, either with progressive decay, under the action of infra-red radiation, or with a temperature change, and it would not seem probable that the effect of either infra-red or temperature would be the same on each component of a complex band. Ives and Luckiesh[3], too, have shown that the effect of infra-red is one of total emission and not of a separate band or part

[1] Phys. Rev., **32**, 38 (1911).
[2] Phys. Rev., **32**, 115 (1911).
[3] Astrophys. J., **34**, 173 (1911); ibid., **36**, 330 (1912).

of the radiation, although they point out that the intensity of the phosphorescence is directly proportional to that of the red or infra-red radiation causing the abnormal decay.

Here again the general evidence so far forthcoming is conflicting and at times contradictory. Lenard[1] and his co-workers have shown definitely that, in the phosphorescence, three different processes may be distinguished, one of very short duration, one of medium duration and one of very long duration. Such being the case it is not to be expected that the direct observations as made should bear of a very simple explanation.

It was proposed therefore to study again the effect of temperature, over a limited range, on the rate of decay of zinc sulphide phosphorescence and to compare this rigorously with the action of radiation as Perrin suggests.

Experimental and Results

The method adopted in obtaining the temperature coefficient of phosphorescent decay was to measure the time taken for a sample of zinc sulphide, saturated with the exciting radiation, at a known fixed temperature, to decay to a fixed photometric standard. The comparison between the intensity of the zinc sulphide screen and that of the standard was made possible by use of a photometer in which the screen was viewed directly through a circular glass plate which carried at its center a small right-angled prism, the latter reflecting the light of the photometric standard. The field of view thus obtained was a square of fixed color and intensity surrounded by the light from the phosphorescing screen. When the field presented an even appearance the intensity of the phosphorescence was identical with that of the standard. The arrival at this point was accurately observable by the disappearance of the line of demarcation between the two lights.

The arrangement of the apparatus was as follows: the zinc sulphide screen was enclosed in an oven, the temperature of which was automatically regulated to $\pm 0.1°C$. The oven carried two windows, one of glass through which the phosphorescence was observed and one of quartz so that the exciting radiation when necessary could be in the ultra-violet region. A shutter was placed immediately in front of this latter window and served to cut off the exciting light as desired. Observation of the phosphorescence was made as stated, through the photometer using a solution of suitable color illuminated by a small electric light as standard for comparison.

The samples of phosphorescent zinc sulphide were five in number. Three, containing copper, exhibited a bluish green phosphorescence; the fourth was yellow, whilst the fifth had a distinctly red phosphorescence. The samples were obtained from various sources and their composition and method of preparation was not known.

As sources of exciting radiation the Kromayer quartz mercury lamp was used for ultra-violet alone, the visible being excluded by means of a nickel glass screen. For visible radiation as exciting source two tungsten filament

[1] Ann. Physik, **1904** et seq.

lamps (250 watts) were used, one with a plain glass bulb and the other with a blue glass bulb, the familiar day-light lamp, which transmitted therefore less red light than the former.

The experimental procedure consisted first in allowing the sulphide screen at a fixed temperature to become saturated with the exciting radiation, which was then cut off by means of the shutter, at the same instant a stop-watch being released. The moment that an even field was obtained in the photometer, was registered on the watch and the interval for the decay of phosphorescence noted. This measurement was then repeated from ten to twenty times and the average value at that temperature taken. The temperature of the oven was then raised a known amount and the process repeated using the same intensities of radiation for both the exciting source and photometric standard as at the lower temperature. In this manner the times of decay were obtained at a series of temperatures from room temperature to 110°C. The same process was then repeated using the other sources of excitation and the temperature coefficients found under the different conditions. Other samples of zinc sulphide were then substituted and similar measurements made.

Table I gives the times of decay to standard intensity for the various samples at the temperatures indicated. The graph accompanying these, Fig. 1, is typical of the others.

TABLE I

Times of Decay in Seconds

Zinc Sulphides

Temp. °C	Green A Kromayer Lamp	Green A Tungsten Lamp	Green A Daylight Lamp	Green B Tungsten Lamp	Green C Tungsten Lamp	Yellow Tungsten Lamp	Red Tungsten Lamp
25		19.00	10.60	24.00	23.00	11.80	8.40
30	7.40						
35		16.60	9.00	20.00	20.40	10.60	7.40
40	6.31						
45		14.20	7.60	17.05	18.30	9.60	6.60
50	5.40						
55		12.15	6.30	14.40	16.40	8.60	5.80
60	4.55						
65		10.20	5.10	12.20	14.40	7.80	5.00
70	3.80						
75		8.30	4.00	10.00	12.60	6.90	4.40
80	3.10						
85		6.45	3.10	8.00	10.80	6.20	3.80
90	2.55						
95		4.90	2.30	6.20	9.20	5.60	3.40
100	2.00						
105		3.40	1.60	4.60	7.80	5.20	3.00
110	1.60						

The average temperature coefficients corresponding to these times of decay and calculated directly from them are given in the following table.

TABLE II

Sample and Exciting Source	Mean Temp. Coef.
Green A. Kromayer Lamp.	1.20
Green A. Tungsten Lamp.	1.24
Green A. Daylight Lamp.	1.25
Green B. Tungsten Lamp.	1.25
Green C. Tungsten Lamp.	1.15
Yellow. Tungsten Lamp.	1.12
Red. Tungsten Lamp.	1.14

The reliability of these mean values may be seen from the detailed calculations shown in Table III which gives the temperature coefficients per 10°C throughout the range of temperatures studied.

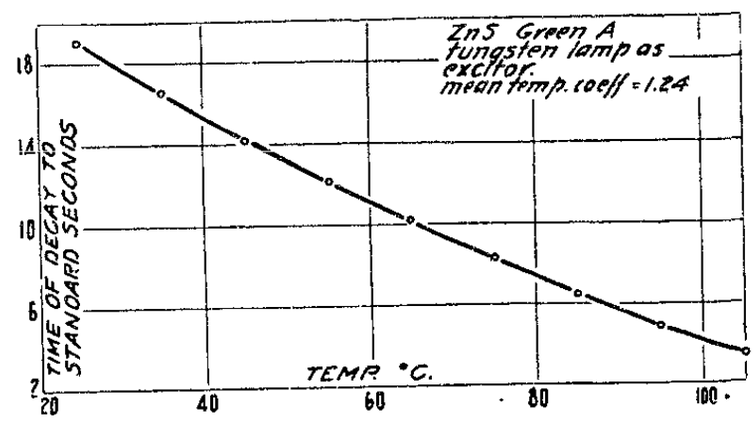


FIG. 1

TABLE III

ZnS. Green A. Kromayer Lamp as Excitor

Temp. Range in °C	Temp. Coef.	Temp. Range in °C	Temp. Coef.
30-40	1.17	70-80	1.23
40-50	1.17	80-90	1.21
50-60	1.19	90-100	1.28
60-70	1.20	100-110	1.25
		Mean	1.20

The variation of these values from the mean may be either real or apparent, that is to say, there may actually be a variation in the temperature coefficient, or, the error involved in the measurement of the times of decay at the higher temperatures, which is of the order of two seconds, may account for it. That the former is more probably the case is suggested first by the results themselves, in the general rising trend of the temperature coefficients with a rise in temperature, shown not only in the instance quoted but in every case studied. Secondly, the work of Lenard already mentioned, having shown the complexity of the total phosphorescent process, would suggest a change in the temperature coefficient with a change in temperature since in all probability the long and short phosphorescences will not have the same temperature coefficient and one or other would predominate at the higher temperatures.

As regards the actual measurement of the time of decay even at the higher temperatures where the times are short, the general smoothness of the curves obtained may be taken as qualititative evidence of their reliability. Actually however the degree of precision for the average of the twenty readings taken at one temperature is ±5 percent at the higher t mperatures and may fall to as low as ±1 percent at room temperatures where the times are much longer.

The similarity then, between the temperature coefficients of decay in the first three instances in Table II where the same sample of zinc sulphide was used and the same photometric standard used for comparison indicates that a change in the source of exciting radiation is without any appreciable effect on the phosphorescent process.

That the phosphorescence itself is complex may be indicated by a study of the same sample using a different standard for comparison. The following table gives the times of decay for the sample Green A using a more feeble intensity in the photometer for comparison. The times it will be noted are therefore much longer.

TABLE IV

ZnS. Green A. Tungsten Lamp as Excitor

Temp. °C	Time of decay. Seconds	Temp. °C	Time of decay. Seconds
25	10.80	75	5·35
35	9·50	85	4·50
45	8.35	95	3·70
55	7·30	105	3.00
65	6.30		

The mean temperature coefficient calculated from these values is 1.18 as compared with the value 1.20 obtained from a study over a shorter period of the phosphorescence. The same effect namely a slightly lower temperature coefficient was observed in two other cases studied when a more feeble standard was used for comparison, which would point to the fact that the phosphorescent process of long duration had a lower temperature coefficient than the process of shorter duration. This in turn is in line with the increase in temperature coefficient with an increase in temperature since it is the phosphorescence of shorter duration which is more affected by an increase in temperature.

The temperature coefficients for the different samples as shown in Table II would suggest that there exists some relation between the color of the phosphorescence and the temperature coefficient. The results 1.12 for the sample phosphorescing yellow and 1.14 for the red, are both lower than the green samples. Remembering that the temperature coefficient is lowered in general by an increase in the period of decay studied there would appear to be a progressive fall in the temperature coefficient as the phosphorescence passes from green to red. It is hoped at a later date to study this problem further.

The feature of prime importance however, which these results have brought out is the order of magnitude of the temperature coefficient of decay. If we take the value 1.20 as a mean value of all the samples, the smallness of

this as a temperature coefficient is remarkable. Such a value is at once suggestive of a photochemical process rather than of a thermal process, and is much lower than the figure quoted by Perrin. Using the simple radiation theory in the manner previously suggested we find that the temperature coefficient of 1.20 corresponds to 4300 calories in the mean temperature range 65-75°C, or to a wave length 6.65μ in the short infra-red. The difference between this value 6.65μ and that which Perrin gives, namely 1μ, calls immediately for explanation.

Perrin tells us that on exposing an illuminated zinc sulphide screen to a spectrum of radiation the spot hit by the rays of wave lengths 0.7 to 1.5μ phosphoresces more brilliantly than the rest and eventually becomes dark. The uncertainty of definitely identifying the wave length of a band in such a crude experiment suggests at once that the region was probably much larger and that even though a very narrow band was responsible for the darkening, the overlapping of spectra would cause an apparent broadening. It seemed advisable therefore to try the effects of practically monochromatic radiation at various points in the spectrum and thereby to isolate the effective wave length, if such exists.

The first wave length tested was that calculated from the temperature coefficient namely, 6.65μ. This was obtained by means of a Hilger Infra-red Spectrometer using a carbon arc as source of illumination and rock salt prism as dispersing agent. The intensity of the practically monochromatic radiation at 6.65μ although feeble was still sufficient to cause a more rapid decay of the phosphorescence of the zinc sulphide screen, as shown by a black line—the image of the spectrometer slit—on the faintly phosphorescing background. The result appears then, to be in agreement with the radiation theory. On turning the prism, however, almost indiscriminately, it was found that the same result was obtainable at any wave length in the short infra-red. Apparently a single frequency of radiation is not alone active, and it was decided to try the effects of various screens.

The first screen was the biotite mica screen used previously[1] which transmitted radiation from about 2μ up to 8μ only. The zinc sulphide screen was illuminated over its whole surface, half of it was then covered and the remaining half exposed to the infra-red radiation for a few seconds. It was found that the half which had been exposed was much darker than the unexposed portion.

In order to pass further into the infra-red it was necessary to find a screen which absorbed in the near infra-red but which became transparent again in the further region. It seems remarkable that sphalerite itself is such a substance. Coblentz[2] states that a crystal 1.5 mms. thick is transparent from 5μ to 12μ and is entirely opaque at 15μ. A thin plate of sphalerite was obtained and used as a filter in a manner similar to the biotite. The result was again the same, showing that apparently any wave length in the short infra-red is capable of causing a more rapid decay of the phosphorescence.

[1] J. Am. Chem. Soc., **48**, 577 (1926).
[2] Carnegie Inst. Pub., No **65** (1906).

Using a ruby glass filter the result was likewise the same, that is there was a more rapid decay of the phosphorescence and the part exposed to the red light was darker than the unexposed portion. A yellow filter obtained by interposing a solution of picric acid in water between the light source and the phosphorescing screen also caused a darkening more rapidly than with the normal rate of decay.

In all these cases the sample of zinc sulphide used had been the sample A which phosphoresced green. A green filter was therefore used to see what the effect would be. The filter was identical with the one which had been used as the comparison standard in the photometer in the previous experiments and was a solution of nickel and copper nitrates in water. It was found that when the light filter was sufficiently concentrated to give a color on the non-phosphorescing zinc sulphide, of the same intensity as the normal phosphorescence without the filter, then practically no phosphorescence of the screen was caused and no increased darkening was observed with the phosphorescing screen. If this filter is diluted with water, some phosphorescence is caused, presumably owing to the shorter wave lengths which are transmitted by the more dilute filter. If however, the filter is made more concentrated, an increased darkening action can be observed with a zinc sulphide screen which is already phosphorescing.

From these experiments it is apparent, first, that Stokes' Law is being obeyed, and second, that any radiation of wave length shorter than the mean phosphorescent wave length is capable of causing a more rapid decay of the phosphorescence.

This is further confirmed by experiments with the other samples of zinc sulphide which phosphorescence at different regions. Taking (1) the green sample A, (2) the yellow and (3) the red phosphorescent zinc sulphides and constructing light filters of (1) nickel and copper nitrates (2) picric acid and (3) potassium dichromate solutions respectively, such that the light transmitted by these was of approximately the same intensity as the normal phosphorescence of each of the three samples, it was found that the green filter (1) though without action on the green sample was capable of causing phosphorescence of both the yellow and red samples of zinc sulphide. Filter (2) of picric acid would cause the red zinc sulphide alone to phosphoresce, but also caused a darkening of the phosphorescing green sample more rapidly than normal. Filter (3) of potassium dichromate whilst inactive towards the zinc sulphide which phosphoresced in the red was capable of causing a more rapid decay of the phosphorescence of both the green and yellow samples.

It is obvious then that the line of demarcation between ability to cause phosphorescence and ability to cause the decay of phosphorescence is quite sharp. Wave lengths shorter than this line will all cause phosphorescence whilst all wave lengths longer than this line will cause a more rapid decay. The requirements of the simple radiation theory are not at all satisfied.

What the true explanation of these results is, it is hoped to make the subject of a subsequent paper. The fact that the magnitude of the temperature coefficient would seem to point to a photochemical rather than a thermal

reaction suggests that a physical explanation is probable, and that purely chemical effects only enter in cases of extreme illumination such as the blackening of zinc sulphide by intense ultra-violet light, as studied in detail by Lenard[1]. There, the bond between the atoms in the molecule is completely severed and free zinc remains. That such a profound change is required for phosphorescence does not seem likely, rather would an electron shift within the zinc sulphide molecule account for the results.

Summary

1. The contradictory nature of the data on the effect of temperature on the rate of decay of zinc sulphide phosphorescence is pointed out.

2. The temperature coefficient of the rate of decay of phosphorescence has been measured for five different samples of zinc sulphide under varying conditions.

3. Analysis of the data shows the temperature coefficient to be 1.20 per 10°C in the neighborhood of 70°C corresponding to a wave length of 6.65μ on the basis of the radiation theory. The difference between this and Perrin's figure of 1μ has been noted.

4. It has been shown that the abnormal decaying effect of radiation on zinc sulphide phosphorescence is not confined to a particular frequency, nor to a particular region of the spectrum, but that all frequencies incapable of causing phosphorescence will cause its more rapid decay. Further work is in progress.

New York, N. Y.

[1] Ann. Physik, **68**, 553 (1922)

THE METHANE EQUILIBRIUM. II

BY R. C. CANTELO

It is quite conceivable that when ethylene is subjected to thermal decomposition, we might have any or all of the reactions indicated below, proceeding either simultaneously or successively. For convenience, the equations have been written in such a way that the left-hand side is a single hydrocarbon.

$$(1) \quad C_2H_4 \rightleftarrows 2\,C + 2\,H_2$$
$$(2) \quad C_2H_4 \rightleftarrows C_2H_2 + H_2$$
$$(3) \quad 3\,C_2H_4 \rightleftarrows C_6H_6 + 3\,H_2$$
$$(4) \quad C_2H_6 \rightleftarrows 2\,C + 3\,H_2$$
$$(5) \quad C_2H_6 \rightleftarrows C_2H_4 + H_2$$
$$(6) \quad C_2H_6 \rightleftarrows C_2H_2 + 2\,H_2$$
$$(7) \quad 3\,C_2H_2 \rightleftarrows C_6H_6$$
$$(8) \quad CH_4 \rightleftarrows C + 2\,H_2$$
$$(9) \quad 2\,CH_4 \rightleftarrows C_2H_4 + 2\,H_2$$
$$(10) \quad CH_4 \rightleftarrows C + 2\,H_2$$

etc.

Now it is quite possible to apply the Phase Rule to such a series of equilibria. At a sufficiently high temperature, the maximum number of phases is two, the gas and the solid, the variants are fixed as temperature and pressure; and the number of components is evidently two. Hence the equation $N-R+2=V$ is satisfied. (N = no. of components, R = no. of phases, and V = the variants.) The conclusion is reached therefore, that whether the initial system be methane, ethylene, or ethane, the final system must be one in equilibrium. This system may consist of any or all of the substances indicated, but each of these compounds must be present in such a proportion as to present a "symphony of equilibria" amongst them all.

The question now arises whether it is possible to predict the quantitative composition of the equilibrium system for a definite temperature and pressure. To answer this question it is necessary to turn to Thermodynamics for criteria of equilibrium and the simplest is evidently the free energy function. Gibbs[1] states that for any isothermal and isobaric process

$$(\delta\zeta)_{T.P.} \geqq 0$$

i. e., the free energy is continually tending towards a minimum; and finally for a system in neutral equilibrium, the free energy change is zero.[2]

Now if it were possible to calculate the free energy decrease attending the synthesis of each of the hydrocarbons considered above, it could be said that where the decrease is positive, the final system is the stable one; and where, on the other hand, the free energy had increased, it would be necessary to state

[1] "Thermodynamics," 91 (1906).

[2] This is really Gibbs' Thermodynamic Potential.

that the final system was an unstable one. For example, Lewis and Randall[1] have calculated the free energy decrease ($-\triangle F$) attending the synthesis of methane from graphitic carbon and hydrogen, and find it to be $+12{,}800$ calories. This means simply that methane is a stable compound, a fact borne out by numerous experimental investigations. No such data exist for the other compounds considered above.

But it is not necessary to stop at this point. The free energy of such a reaction as

$$aA + bB + \text{——} \rightleftarrows eE + fF + \text{——}$$

is given by the expression

$$-\triangle F = RT \left\{ \ln K_p - \ln \frac{p'^{e}_{E} \cdot p'^{f}_{F}}{p'^{a}_{A} \cdot p'^{b}_{B}} \right\}$$

which, as shown, involves the equilibrium constant. If now, the pressure quantities in the second term within the bracket be made each arbitrarily equal to 1 atmosphere, the expression simplifies to

$$-\triangle F = RT \ln K$$

So that we have in the equilibrium constant, a criterion for the stability of each of the various systems under consideration.

Again the van't Hoff equation

$$d \ln K_p = \frac{\triangle H}{RT^2} \cdot dT$$

should enable K_p for a given reaction to be calculated when $\triangle H$, the increase in heat content attending the reaction, is known. But the above relation is really a differential equation and its integration will involve some unknown constant of integration. The simplest solution lies in the use of approximate expressions, of which the Nernst Approximation[2] has been most successful.

$$\log K = \frac{-\triangle H}{4.571\, T} + \Sigma v\ 1.75 \log T + \Sigma vC$$

$\triangle H$ = increase in heat content of the system as written in the thermochemical equation.

Σv = change in the number of molecules formed by the reaction.

ΣvC = the summation of the "chemical constants of the reacting substances existing only in the gaseous state."

Table I gives the values for K_p at different temperatures for each of the equilibria considered above. The values for $\triangle H$ were calculated from the heat contents of the various compounds involved.

[1] "Thermodynamics," 607 (1923).

[2] "Experimentelle und theoretische Grundlagen des neuen Wärmesatzes," (1918).

TABLE I

	Reaction	Δ H	Approximate K_{200}	K_{400}	K_{600}	K_{800}
(1)	$C_2H_4 \rightleftarrows 2C + 2H_2$	−14,600	6.9×10^{11}	1.2×10^{10}	1.2×10^{9}	4.8×10^{8}
(2)	$C_2H_4 \rightleftarrows C_2H_2 + H_2$	43,500	3.3×10^{-14}	6.3×10^{-8}	1.8×10^{-4}	2.7×10^{-2}
(3)	$3C_2H_4 \rightleftarrows C_6H_6 + 3H_2$	−32,500	1.3×10^{19}	8×10^{14}	5.1×10^{12}	2×10^{11}
(4)	$C_2H_6 \rightleftarrows 2C + 3H_2$	23,300	6.7	3.2×10^{4}	4×10^{6}	1.2×10^{8}
(5)	$C_2H_6 \rightleftarrows C_2H_4 + H_2$	37,900	8.7×10^{-12}	2.8×10^{-6}	2.1×10^{-3}	1.9×10^{-2}
(6)	$C_2H_6 \rightleftarrows C_2H_2 + 2H_2$	81,400	3×10^{-25}	1.7×10^{-13}	6.6×10^{-7}	7×10^{-3}
(7)	$3C_2H_2 \rightleftarrows C_6H_6$	−163,000	2.6×10^{59}	3.1×10^{36}	7.6×10^{23}	10^{22}
(8)	$CH_4 \rightleftarrows C + 2H_2$	18,900	6.4×10^{-4}	3.2×10^{-1}	13	142
(9)	$2CH_4 \rightleftarrows C_2H_4 + 2H_2$	52,400	3.1×10^{-19}	8.9×10^{-12}	1.2×10^{-7}	2.4×10^{-4}
(10)	$2CH_1 \rightleftarrows C_2H_2 + 3H_2$	95,900	1.6×10^{-32}	6.4×10^{-19}	2×10^{-11}	1.2×10^{-6}

It must be emphasized that no single reaction may be considered exclusively by itself. *All* the above reactions must be considered as vitally interrelated, and the calculated values of K_p must be reviewed with respect to all possible systems.

A consideration of reactions (1), (2), (3), (5), (9) shows that the initial system ethylene tends to pass to an equilibrium system involving carbon, hydrogen, ethane, benzene, and methane.

Reactions (4), (5), (6), (8) show that the initial system ethane tends to pass to an equilibrium system, carbon, hydrogen, and methane; but ethane is fairly stable up to 400°C.

Reactions (8), (9), (10) show that the sole tendency in the temperature interval 200-800°C. is for the initial system methane to pass to the final system (in equilibrium) methane, carbon, and hydrogen.

There is little tendency in these three systems to give acetylene (at equilibrium) so that equation (10) need not be considered.

The question now arises whether benzene will be stable over this temperature interval.

$$C_6H_6 \rightleftarrows 6\ C + 3\ H_2$$
$$K_{200} = 2.5 \times 10^{16}$$
$$K_{500} = 5 \times 10^{14}$$

These values indicate that benzene should not exist over this temperature interval. In this connection it is interesting to note that Sabatier[1] states with respect to the direct hydrogenation of benzene in the presence of metallic nickel that above 200° and especially "au delà de 300°, une partie du benzène est hydrogénée en methane, et il y a dépôt d'un peu de charbon sur le nickel."

It must be emphasized again that the above deductions are based upon the assumption that sufficient time elapses to give an equilibrium state. This may be one second or a million years!

The final conclusion from the above consideration of equilibrium constants is that whether the initial system be methane, ethylene, or ethane, the final equilibrium system will be methane, carbon, and hydrogen in the proportions required to satisfy this equilibrium. But "man kann nicht mathematisch beweisen dass die Natur so sein müsse, wie sie ist." Can the above be shown experimentally?

The next paper of this series will discuss experiments performed with a view to obtaining the methane equilibrium with ethylene as the initial system.

For the present it is interesting to review briefly the more modern work upon the thermal decomposition of ethylene. Bone and Coward[2] carried out what was probably the most valuable investigation on thermal reactions of ethylene. They circulated ethylene for a period of 2½ hours through a tube heated to 570°-580°C. Acetylene, ethane, methane, and hydrogen were produced but the quantity of carbon separated was negligible. Methane ac-

[1] "*La Catalyse en Chimie organique*," 171 (1920).

[2] J. Chem. Soc., **93**, 1197 (1908).

cumulated during the first 60 minutes and then decreased slightly; acetylene varied irregularly from 12% of the gases after two minutes heating to 6% of the gases at the end of the experiment.

The importance of the time factor is shown especially well in Table II taken from their work on the decomposition of ethylene at 800°C.

TABLE II

Time in minutes	1	5	15	60
% C_2H_2	3.00	23.9	3.85	nil
% C_2H_4	57.25	1.4	9.65	0.9
% C_2H_6	3.25	5.0	1.3	nil
% CH_4	29.4	53.4	64.45	67.7
% H_2	7.1	17.0	20.75	31.4

It is evident that this table adds confirmation to the theoretical conclusions of the writer.

When ethylene was heated to 950°C., 90% decomposed within one minute, and all was decomposed after 15 minutes. Small amounts of aromatic hydrocarbons were produced, but large quantities of carbon separated. The gases were methane and hydrogen. At 1100°C., ethylene was rapidly and completely decomposed into carbon, methane, and hydrogen.

Sabatier and Senderens[1] have studied the thermal decomposition of ethylene in the presence of catalysts.

When ethylene was passed with moderate rapidity, over nickel obtained from its oxide by hydrogen, and heated to a temperature not exceeding 325°C., the issuing gas was a mixture of 10 volumes of hydrogen with about 60 volumes of ethane and 30 volumes of methane. At higher temperatures the proportion of ethane diminished and only traces remained when the temperature was that of red heat. It appeared that the first change in the decomposition was the formation of carbon and ethane, the latter at higher temperature decomposing into carbon and hydrogen. Direct experiments showed that ethane was partially decomposed by nickel at 325° and that methane was decomposed especially above 390°C.

Sabatier also makes the statement:—"Avec une colonne assez longue de nickel reduit, ou un courant suffisamment lent d'ethylène, on peut arriver dès 325° à une transformation à peu près complète en formène, mêlé d'un peu d'hydrogène. Il serait beaucoup moins aisé d'attendre la décarburation totale du formène, celle-ci n'étant pas encore très rapide au rouge sombre." The following statement should also be quoted as it has a confirmatory bearing upon the theoretical conclusions:

"Les gas recueillis ne contiennent pas en proportion appreciable de gas absorbable par le brome, et ne donnent pas de réaction avec la solution ammoniacal de chlorure cuivreux: ils ne renferment donc aucunes doses mesurables

[1] Compt. rend., **124**, 616, 1358 (1897); **131**, 267 (1900).

de carbures ethylèniques ou acétylèniques. Ils sont constitués par un mélange d'hydrogène et de carbures formèniques." Again "dans aucun cas . . . nous n'avons pu condenser dose perceptible de produit liquide."

Finely divided platinum and copper have no action on ethylene below 400°C., but cobalt above 300° partially decomposes it into ethane, methane, and hydrogen together with carbon, but without any acetylene. Iron above 350°C. has less action but decomposes a part of the gas into ethane, hydrogen, and carbon.

When a mixture of hydrogen with an excess of ethylene is passed over reduced nickel heated to a temperature not exceeding 150°C, ethane is the sole product of the reaction. This reduction of ethylene to ethane at 150°C., furnishes an interesting example of the utility of the calculated equilibrium constants in prophesying the course of a reaction.

$$C_2H_6 \rightleftarrows C_2H_4 + H_2 - 37{,}900$$

$$K_{150} = \frac{P_{C_2H_4} \cdot p_{H_2}}{p_{C_2H_6}} = 6 \times 10^{-14}$$

That is, the numerator is exceedingly small, indicating complete transformation to ethane.

On account of the fact that ethane is usually formed by the thermal decomposition of ethylene, the work of Bone and Coward[4] on the thermal decomposition of ethane should be mentioned at this point.

In one experiment ethane was circulated through a tube heated to 675°C. The results of this experiment are given in Table III.

TABLE III

Times in hours	C_2H_2	C_2H_4	C_2H_6	CH_4	H_2
0.5	4.1	24.7	34.7	8.4	28.1
1.5	5.1	24.1	9.8	19.9	41.1
3.0	2.8	16.4	7.3	32.9	40.6
6.0	1.9	0.7	2.0	54.5	40.9

At 800°C., ethane decomposes rapidly. In one minute's heating, the gas had the composition acetylene, 1.9%; ethylene, 11.2%; ethane, 17.9%; methane 31.3%; and hydrogen, 37.7%. After one hour's heating, only methane and hydrogen remained. Similar results were obtained at the higher temperatures.

A perusal of the above brief review of the work upon ethylene and ethane shows that the conclusions drawn by the writer from the calculated equilibrium constants, are supported by experimental investigations. As Bone has pointed out, in the majority of investigations, the time factor has been neglected. His own work, however, shows that with increasing time, the initial system approaches nearer and nearer to neutral equilibrium.

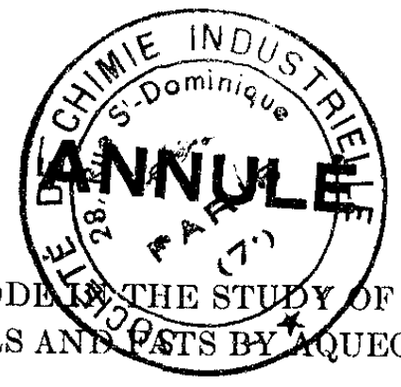
Summary

Calculations of equilibrium constants for the possible reactions involved in the decomposition of methane, ethylene, and ethane indicated that above 400°, the final system should be one of methane, carbon, and hydrogen, irrespective of which hydrocarbon was used as the initial system.

A review of the literature on the decomposition of ethylene and ethane, both by heat alone and in the presence of catalysts, showed that the experimental results of previous investigators were in harmony with the conclusions drawn from the calculated equilibrium constants.

Department of Chemistry,
University of Cincinnati,
Cincinnati, Ohio.

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131

THE HYDROGEN ELECTRODE IN THE STUDY OF THE RATE OF SAPONIFICATION OF OILS AND FATS BY AQUEOUS ALKALI

BY J. W. McBAIN, H. S. HOWES AND MURIEL THORBURN

The only available measurements of the rate of saponification of triglycerides or commercial oils and fats by aqueous alkali are those of Norris and McBain[1] and of H. Langton.[2] Measurements of this type are, however, all open to the serious criticism that when the reaction is allowed to proceed from beginning to end, numerous changes of state occur. Thus, inspection of the diagrams of phase rule equilibria of soaps now available shows that six different sets of phases may be present at different stages of the reaction. Not only so but the concentrations of all the substances are continually changing including any emulsifiers as well. Hence, there are insufficient data available upon which to judge whether it might be industrially preferable to carry out saponification in "crutchers" with concentrated alkali before putting the resulting soap into the soap pan.

Previous work showed that the rate of reaction is almost entirely dependent on the rate of movement of alkali to and of the products of reaction from the surface of the droplets of oil, and it indicated the factors which are involved and even some of their effects. However for any real advance it was necessary to devise a new method such as is described in the present investigation.

It has been found possible to vary one factor at a time keeping all the others constant[3] and thus to isolate and determine the effect of each factor. Each of the reagents except the hydroxide is kept in sufficiently large excess to be appreciably constant throughout any one experiment thus keeping all the physical, as well as chemical factors, constant.

It is found that the hydrogen electrode is actually able to follow the rate of disappearance of the dilute hydroxide. This obeys a monomolecular law in so far as hydroxyl ion is concerned and the results are surprisingly reproducible. We have thus a rapid and quantitative method for measuring the rate of saponification under all conditions. The quantitative information here obtained substantiates the conclusions indicated in the previous communication. It is now a simple task to extend these results so as to obtain representative data for a large number of pure triglycerides as well as commercial materials. The results here recorded refer chiefly to coconut oil together with a few data for trilaurin and tripalmitin.

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[1] J. Chem. Soc., **121**, 1362 (1922). Treub has called our attention to papers by himself (J. Chim. phys., **16**, 107 (1918), Rec. Trav. chim., **42**, 556 (1923). However, they do not contain any actual measurement of rate, but only surmise and mathematical formulations which in part do not find confirmation in our experiments.

[2] J. Oil and Colour Chem. Assocn., **5**, 41 (1922).

[3] Compare Lash Miller: Trans. Roy. Soc. Canada, (3) **2**, 245 (1908); Harcourt and Esson: J. Chem. Soc., **20**, 460 (1866).

Experimental

Chemicals used.

Standard solutions of sodium hydroxide were made by dissolving sodium drippings, free from carbon dioxide, in boiled out distilled water. The solutions were standardised by titration against standard hydrochloric acid (made by the method of Hulett and Bonner[1]) and kept in flasks fitted with vaselined stoppers.

The oils used were of two kinds—pure and commercial. The pure triglycerides, trilaurin and tripalmitin, were supplied by Kahlbaum. The commercial coconut oil used was obtained through the kindness of Chris. Thomas and Bros. Ltd, and had been carefully neutralised by them. On keeping for many months however, it tended to become very slightly rancid and was therefore again neutralised before use by heating with aqueous sodium hydroxide, and was subsequently washed free from alkali with boiling distilled water.

Sodium laurate and sodium palmitate were obtained from Kahlbaum. Coconut oil was saponified with alcoholic sodium hydroxide, and soap formed was decomposed with sulphuric acid and the fatty acids thoroughly washed with boiling water and dried at 100°. From them coconut oil soap was prepared by the method of Bunbury and Martin.[2]

Method of measurement of rate of reaction.

The hydrogen electrode was coupled with a decinormal calomel electrode as follows:—

$Pt\ H_2$	Sapon^n. mixture	½ satd. KCl	½ satd. KCl	0.1N_v KCl satd. with Hg_2Cl_2	Hg_2Cl_2 (solid)	Hg
90°	90°	90°	room temp.	room temp.	room temp.	room temp.

As the potential of the calomel electrode remains constant throughout, the rate of change of E. M. F. of this cell is nearly proportional to the rate of saponification as is shown below, under the heading "Calculation of Results."

Apparatus employed.

Saponification was carried out in a Pyrex, three-necked, round-bottomed flask of 500 cc. capacity (see Fig. 1). A stirrer passed through the middle neck. It consisted of a small silver propeller (made from a silver disc) bound on the end of a glass rod with silver wire, and was driven at a constant speed of 2400 r. p. m. by a small A. C. induction motor. The speed was frequently checked by a tachometer. The other two necks were utilised for the hydrogen electrode and the connection to the calomel electrode respectively. The reaction flask was about three-quarters immersed in a thermostat at 91° (±0.10) the surface of which was covered with melted paraffin to prevent evaporation.

The hydrogen electrode was a slightly modified form of the Hildebrand type (see Fig. 1a). It was made by welding platinum wire to a piece of plat-

[1] J. Am. Chem. Soc., **31**, 390 (1909).
[2] J. Chem. Soc., **105**, 417 (1914).

133

inum foil about 1 cm. square and sealing the wire into a narrow-bore glass tube. This tube was two-thirds filled with mercury and connection made by an amalgamated copper wire dipping into the mercury. The outer glass tube was made of glass tubing of about $\frac{1}{2}''$ bore. It was closed at the top by a rubber stopper through which passed the inside tube. A small side-tube, sealed at right angles to the large outer tube just below the rubber stopper admitted hydrogen. Three circular holes about 1 cm. in diameter at the bottom of the large outer tube provided the hydrogen exit and enabled the reaction mixture

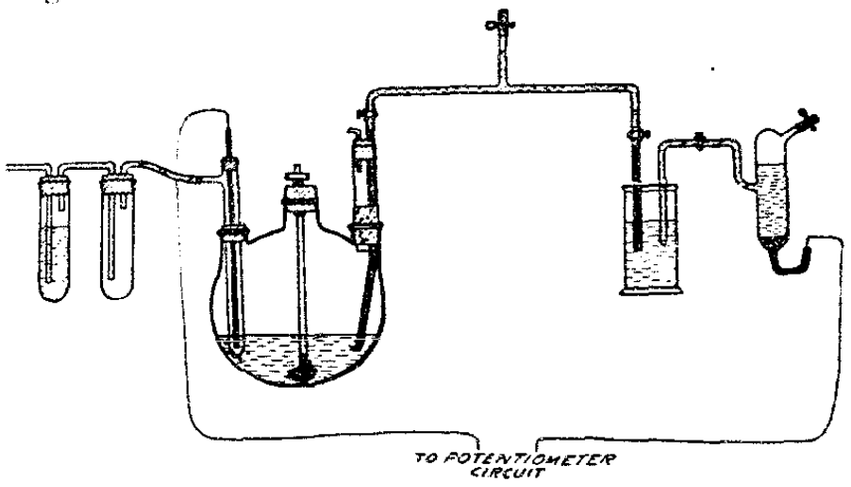


FIG. 1
Diagram of apparatus used.

to have free access to the platinum foil (see Fig. 1a). The electrode was cleaned by electrolysing it as anode in 3N hydrochloric acid solution, and then platinised by making it alternately anode and cathode with another platinum electrode in a solution of platinic chloride. An E. M. F. of four volts was used and the deposit of platinum black obtained was very fine and thin. Occluded chlorine was then removed by immersing the electrode in a solution of acidified ferrous sulphate and it was finally well washed with distilled water. The electrode did not require replating; it was cleaned in hot acid dichromate solution after each experiment and when not in use was kept in distilled water.



FIG. 1a
Section of hydrogen electrode.

The hydrogen supply was kept constant by means of a screw clip on a rubber tube which connected with a screwvalve of a cylinder of hydrogen. The hydrogen was allowed to pass through a safety flask and a flow indicator, and was saturated with water vapour by passing through a tube containing $0.1N_w$ sodium hydroxide at 90° (i. e. a solution of the same concentration as the alkali initially present in the reaction flask) from which it passed through a spray trap to the hydrogen electrode and thence bubbled through the reaction mixture. A small tube for the outlet of hydrogen passed through the cork of the second side neck of the reaction flask, which also carried the capillary siphon filled with half-saturated potassium chloride that formed the connection between the reaction mixture and an ordinary calomel electrode. The end of the capillary that dipped into the flask was drawn out to a fine

upturned point in order to avoid undue mixing of the potassium chloride with the reaction mixture. To lessen vibration of the capillary, an extension consisting of an ordinary piece of glass tubing was fitted to the neck carrying the capillary siphon (see Fig. 1).

A pyknometer calibrated to contain the required weight of $0.3N_w$ sodium hydroxide saturated with hydrogen at room temperature was used for measurement of the sodium hydroxide added to the reaction mixture.

For measurement of E. M. F. the ordinary compensation method of Poggendorf was used except that it was found more convenient to use a voltmeter instead of the usual standard cell. This was a Weston D. C. model and read to 0.001 volt. A capillary electrometer of the Lippmann type was used in obtaining the balance (see Fig. 1b).

Experimental procedure.

In each experiment in this investigation the effect of the concentration of oil and of soap was kept constant by initially adding both these constituents in large excess of the concentration of alkali. The rate during any given experiment was then proportional to the concentration of one reactant only (the alkali); it was then found to be a monomolecular reaction. Each experiment was carried out on a basis of 50 grams of water. Two thirds of the water was added with the soap and one third with the sodium hydroxide. All concentrations are expressed in weight normalities (the number of gram mols associated with 1000 grams of water).

Before every experiment the hydrogen electrode was tested in $0.1N_w$ sodium hydroxide at room temperature as follows:—

Pt H_2	$0.1N_w$ NaOH′	½ satd. KCl	$0.1N_v$ KCl satd. with Hg_2Cl_2	Hg_2Cl_2 solid	Hg

All at room temperature

If, after bubbling hydrogen through for about ten minutes an E. M. F. of about 1.083 volts (theory 1.089) was obtained the electrode was considered to be in order.

The requisite amounts of soap and oil were then weighed into the reaction flask and stirred at 90° for half an hour, hydrogen being bubbled through the whole time to ensure saturation. Meanwhile the hydrogen electrode was allowed to attain equilibrium in a $0.1N_w$ solution of sodium hydroxide at 90°. The potassium chloride siphon was then inserted and the required weight of saturated standard sodium hydroxide heated by placing the pyknometer containing it in the thermostat for about five minutes. It was then poured into the hot mixture of soap and oil, the hydrogen electrode inserted and E. M. F. readings taken every one or two minutes according to the speed of the reaction.

Calculation of results.

Since the progress of the reaction was followed by means of a hydrogen electrode, its E. M. F. is directly proportional to the logarithm of the concentration of hydroxyl ions or inversely proportional to the logarithm of hydrogen

ions, the two being connected through the constant ionic product at the constant temperature. Now for a simple monomolecular reaction the rate constant k should be equal to $1/t$ times the logarithm of the radio of the initial concentration of the hydroxyl ions to that at time t. Hence, since the logarithm of the concentration of hydroxyl ion occurs both in the expression for rate and in the value of the E. M. F., the rate constant is proportional to $1/t$ times the change in E. M. F. up to time t. Therefore if the E. M. F. is plotted against time a straight line should result for a simple monomolecular reaction governed solely by the concentration of the hydroxyl ion. Actually however, although the rate is monomolecular the reaction is incomplete and reversible owing to equilibrium being obtained when the hydrolysis-alkalinity is of the order of 1/1000. Therefore, although the change in E. M. F. is at first proportional to the time, the E. M. F. must ultimately tend to a constant value independent of time corresponding to the hydrolysis-alkalinity. This is illustrated by a typical graph in Figure 2 and we will now proceed to describe a very simple device by which all our results can be integrated without calculation, merely by correcting each point on the curve by amounts shown in Table I below. If the rate is really proportional to the concentration of hydroxyl ion this must result in a straight line as is shown in Fig. 2 and the slope of this straight line is the rate constant.

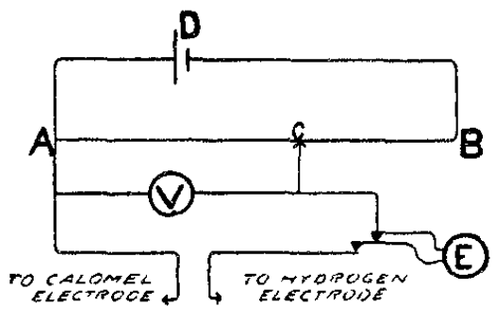


FIG. 1b
Potentiometer circuit.
AB = meter bridge wire.
C = sliding contact.
D = 2-volt accumulator.
E = capillary electrometer.

Let ξ be the equilibrium concentration of OH ions.
" a " " initial " " " " " "
" x " " amount of OH ions reacting in a time t.
k_1 is the velocity constant of the forward reaction.
k_2 " " " " " " back "
The rate observed is $dx/dt = k_1 (a - x) - k_2 x$

Then

$$\frac{1}{t} \ln \frac{a - \xi}{a - \xi - x} = k_1 + k_2$$

Putting the constant $(a - \xi) = n$ and $(a - x) = (OH')t$

$$\ln ((OH')_t - \xi) = \ln n - (k_1 = k_2)t$$

as k_2 is small compared with k_1

$$k_1 + k_2 = k_1 \text{ (approx.)}$$

i.e. $\ln ((OH')_t - \xi) = \ln n - k_1 t = \text{const.} - k_1 t$

Therefore $\ln ((OH')_t - \xi)$ plotted against time should give a straight line to infinity if the reaction behaves as an incomplete or reversible monomolecular one.

$\ln ((OH')_t - \xi)$ expanded

136 $= \ln (OH')_t - \frac{\xi}{(OH')_t} - \frac{\xi^2}{2(OH')^2_t} - \frac{\xi^3}{3(OH')^3_t}$

Now if $(OH')_t = 10$, $\ln ((OH')_t - \xi = \ln(OH')_t - 1/10 - 1/200$

$= \ln(OH')_t - 0.1053$

$= \log_{10}(OH')_t - 0.24255$

0.24255 is thus the vertical error on a log (OH') : t graph where $\frac{(OH')_t}{\xi} = 10$

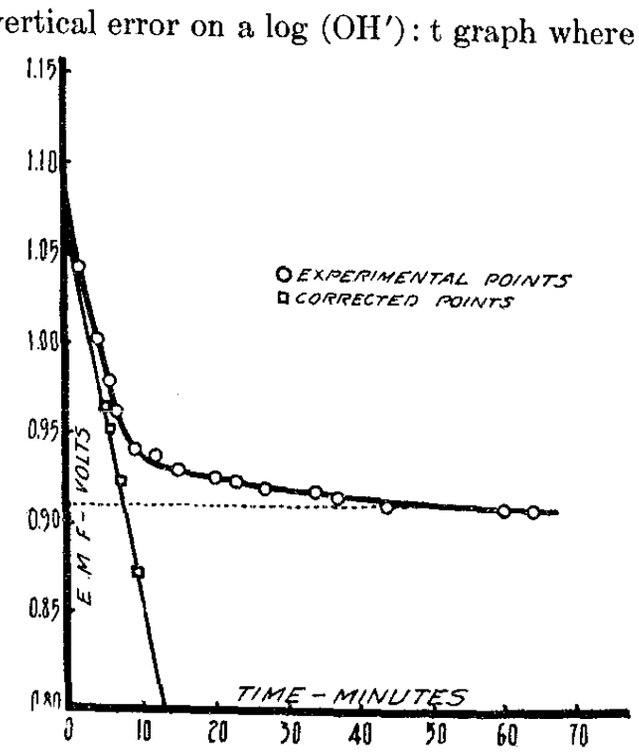


FIG. 2

Typical time/E. M. F. graph with 2 N_w coconut oil soap, 1 N_w coconut oil and 0.1 N_w NaOH at 90° showing correction for hydrolysis.

It is now necessary to express this vertical error in terms of E. M. F.

$E_{(corr.)} = E_{(obs.)} +$ (barometric correction $-$ (correction to normal H_2 electrode from calomel electrode)

$E_{(corr.)} = 0.0001985\ T \log 1/(H')$

$= 0.0001895 \cdot 363 \cdot \log 1/(H')$

$= 0.07206 \log 1/(H')$

But (H') times $(OH') = K_w$

Therefore $E_{(corr.)} = 0.07206 \log (OH')/K_w$

$= 0.07206 (\log(OH') - \log K_w)$

Let E_ξ be the hydrolysis E. M. F.

Then $E_\xi = 0.07206 \log \xi - 0.07206 \log K_w$

and $E_{(obs.)} = 0.07206 (\log(OH')_t - \log K_w)$

therefore $E_{(obs.)} - E = 0.07206 (\log(OH')_t - \log \xi)$

or $\log \frac{(OH')_t}{\xi} = \frac{E_{(obs.)} - E_\xi}{0.07206}$

Correction to $E_{(obs.)}$ is therefore 72.06 times correction to log $(OH')_t$ where $E_{(obs.)}$ is in millivolts.

The following table was drawn up for different values of $(OH')_t/\xi$.

TABLE I

$(OH')_t$	$E_{(obs.)} - E_\xi$ (millivolts)	Correction to log$(OH')_t$	Vertical correction (millivolts)
20	93.75	0.052	3.747
10	72.06	0.24255	17.48
8	65.07	0.307	22.12
5	50.35	0.514	37.04
3	34.38	0.993	71.55

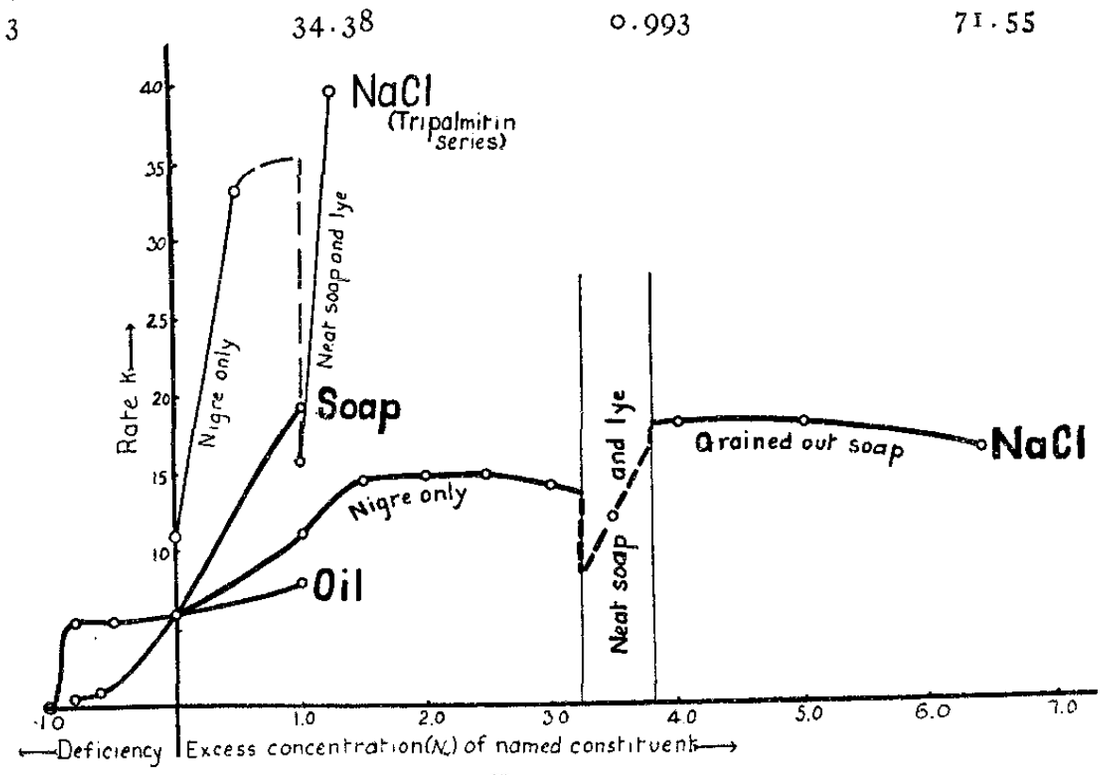


FIG. 3

Dependence of the rate constant (k) upon the concentrations of oil, soap and NaCl respectively. The standard experiment contained 1 N_w oil, 1 N_w soap but no NaCl. Normalities in excess of this are measured to the right and deficiences to the left.

To apply the vertical correction a point is found on the graph where the E. M. F. is greater than the final equilibrium E. M. F. by an amount corresponding to a number in column 2. The corresponding number in column 4 is then the amount by which this point has to be lowered vertically to put it in its corrected position. The slope of the straight line so obtained is the rate constant of the reaction expressed in electrical units. It is seen from Figure 2 that a straight line does result from applying this correction and its slope; namely, 19.25 is the rate constant in *millivolts per minute*.

Experimental Results

Each experiment was carried out at least in duplicate and the results under favourable conditions usually agreed within a few per cent. In the case of some of the later experiments where salting out of the soap took place such close agreement was not possible owing to the thick consistency of the reaction mixture which rendered efficient stirring impossible.

158 The first series of experiments was carried out to test the effect of varying the amount of oil in the reaction mixture. In every case the oil was in sufficient excess for its influence to be constant during any one experiment. The results presented in Table II and Fig. 3 show that the rate constant is greatly dependent upon the first small portion of oil and that it becomes only slightly greater as the amount of oil is further increased. This is very different from the expectations of Treub (loc. cit.), but these actual experiments leave no doubt with regard to this result.

TABLE II (see Fig. 3)

Comparison of the rate of saponification of coconut oil when the concentrations of soap (made from coconut oil) and initial sodium hydroxide are kept constant but the volume of oil is varied.

Soap	Initial concentration of NaOH	Oil	(millivolt k minute units)
$1.0N_w$	$0.1N_w$	$0.2N_w$	5.58
,,	,,	0.5	5.53
,,	,,	1.0	6.0
,,	,,	2.0	8.0

In the second series of experiments the effect of increase of concentration of soap was similar y tested. It will be seen from the results in Table III and Fig. 3 that the increase in the rate constant is more rapid under these conditions than under any others studied.

TABLE III (see Fig. 3)

Comparison of the rate of saponification of coconut oil when the concentrations of oil and initial sodium hydroxide are kept constant but the concentration of coconut oil soap is varied.

Soap	Initial concentration of NaOH	Oil	(millivolt k minute units)
$0.2N_w$	$0.1N_w$	$1.0N_w$	0.75
0.41	,,	,,	1.13
1.0	,,	,,	6.0
2.0*	,,	,,	19.25

*This mixture was so viscous that difficulty was experienced with stirring.

Table IV gives the results of experiments to find the effect of adding glycerine to the initial reaction mixture. A large excess of glycerine lowers the rate constant. The effect however is small in comparison with the proportion of glycerine added. Presumably glycerine slightly diminishes the emulsifying power of soap because the latter is less colloidal in presence of glycerine.

TABLE IV

139

Comparison of the rate of saponification of coconut oil when the concentrations of oil, coconut oil soap, and the initial concentration of sodium hydroxide are kept constant but the concentration glycerine is varied.

Soap	Initial concentration of NaOH	Oil	Glycerine	(millivolt k minute units)
$1.0N_w$	$0.1N_w$	$1.0N_w$	—	6.0
,,	,,	,,	$1.0N_w$	4.7

Table V gives the results of a comparison of the rate of saponification of coconut oil with that of trilaurin. Trilaurin is the chief constituent of coconut oil and, as would therefore be expected, the rate constants are very comparable.

TABLE V

Comparison of the rates of saponification of coconut oil, trilaurin, tripalmitin and tristearin

Oil	Initial concentration of Soap	NaOH	Oil	(millivolt k minute units)
Coconut*	$1.0N_w$	$0.1N_w$	$1.8N_w$	6.7**
Trilaurin*	1.0	0.1	1.8	7.2
,,	1.0	0.1	1.0	7.6†
Tripalmitin*	1.0	0.1	1.0	10.5
,,	1.0	0.1	1.0	10.6†
Tristearin	1.0	0.1	1.0	15.3†

*These results are due to Miss Harrington.
**Interpolated.
†These results are due to A. V. Pitter.

It is seen from Pitter's results (comprising twenty experiments) that the rate of reaction rapidly increases in passing from trilaurin upwards in the homologous series, being doubled when tristearin is reached. This however does not necessarily mean that higher oils and fats are intrinsically more rapidly attacked but must be largely due to the simultaneous change in the soap present as emulsifying agent. In other words the highest soaps are the best soaps at high temperatures. A comprehensive series of experiments will be carried out in which the soap is kept constant and only the oil or fat varied.

In order to test if the size of the platinum electrode affected the results, an experiment was carried out with $1.0N_w$ coconut oil, $1.0N_w$ coconut oil soap and $0.1N_w$ sodium hydroxide using an electrode roughly 50% larger in area than that used in all other experiments. A rate constant of 5.7 was obtained instead of 6.0 (standard experiment).

In all the foregoing experiments two phases only were present during the whole of the reaction, aqueous phase and oil phase, these were maintained in intimate contact by the rapid stirring. In the following experiments salts was added at the commencement of the reaction, rendering the physical state of the mixture much more complex, and in many experiments the viscosity

was increased to such an extent that stirring was impossible. The results are collected in Table VI and VII and are graphed in Fig. 3. The physical state of the reaction mixture and the phases present are described in the last column of each table. The general form of the curve appears to be the same in the case of coconut oil and that of the very different oil, pure tripalmitin, but further experiments are required to confirm the exact shape of the curve.

TABLE VI* (see Fig. 3)

Comparison of the rate of saponification of tripalmitin when the concentrations of oil, sodium palmitate and the initial concentration of sodium hydroxide are kept constant but sodium chloride is added in increasing amounts.

Initial concentration of Soap	NaOH	Oil	Concn. of NaCl	k	Appearance of reaction mixture
$1.0N_w$	$0.1N_w$	$1.0N_w$	—	10.5	
,,	,,	,,	$0.5N_w$	33.3	Homogeneous soap, high viscosity.
,,	,,	,,	1.03	15.8	Heterogeneous soap.
,,	,,	,,	1.25	39.5	,, ,,

*These results are due to Miss Harrington.

TABLE VII (see Fig. 3)

Comparison of the rate of saponification of coconut oil when the concentrations of oil ($1.0N_w$) soap ($1.0N_w$) and the initial concentration of sodium hydroxide ($0.1N_w$) are kept constant but sodium chloride is added in increasing amounts.

Concn. of NaCl	k	Appearance of reaction mixture	Phases
—	6.0	Homogeneous soap solution.	
$1.0N_w$	11.1	Homogeneous soap solution oil in granules	Nigre only
1.5	14.5*	,, ,, ,, ,,	,, ,,
2.0	14.8	,, ,, ,, ,,	,, ,,
2.5	14.8	,, ,, ,, ,,	,, ,,
3.0	14	Heterogeneous soap, oil in granules.	,, ,,
3.5	(12)	,, ,, ,, ,,	Neat soap & lye
4.0**	(18)	,, ,, ,, ,,	Curd and lye
5.0	(18)	,, ,, ,, ,,	,, ,, ,,
6.7 (satd.)	16.2	,, ,, ,, ,,	,, ,, ,,

*When $1.0N_w$ glycerine was present the rate was 12.4 instead of 14.5 thus confirming the result shown in Table IV above.

**It was found difficult to obtain reproducible results between concentrations of $30.N_w$ and $5.0N_w$ sodium chloride, probably owing to the very complicated physical state of the reaction mixture.

Discussion of Results

The results given above are quire sufficient to illustrate that a quick and reliable method has been established for the comparative measurement of rate of saponification in heterogeneous reactions. Further, definite information has been gained with regard to the nature of the reaction.

It is evident from the results of Table II that doubling the amount of oil present does not double the rate constant as might have been expected. Thus we can conclude in accordance with the direct observations of Norris and McBain (loc. cit.) that a given amount of soap has a limited emulsifying action, since the surface of the oil evidently is not proportionately increased when the volume of oil is doubled. It was found that only a portion of the oil was emulsified, the remainder settling out immediately on standing.

This conclusion is supported by the results of Table III which show the effect of increasing the amount of initial soap. The rate constant is rapidly increased up to a concentration of $2N_w$ soap beyond which concentration the reaction mixture becomes so viscous that the experimental method breaks down. The only possible explanation of this increase in rate of reaction is that the oil is more perfectly emulsified when more initial soap is present. This is in accordance with observations of surface tension against oil which is indefinitely lowered as the concentration of soap is increased.

When we consider the results of Tables VI and VII from experiments where salt was added at the commencement of the reaction, the conclusions to be drawn are not quite so certain. It is well-known that soap boilers add solid sodium chloride to their reaction mixture during saponification in order to "salt out" the soap thus rendering the whole mass much less viscous and more manageable. Norris and McBain (loc. cit.) found that the presence of salt sometimes increased the rate of saponification and at other times decreased it according to the kind of oil used, the concentration of salt added and the physical state of the reaction mixture. However, no conclusions could be reached definite enough to enable them to predict the rate under any given set of initial conditions, owing firstly to their inadequate method of experimental procedure to which previous reference has been made, and secondly to the very limited amount of data then available with regard to the conditions governing the equilibria in the complicated ternary system soap: electrolyte: water. Since 1922 however our knowledge in this direction has been greatly increased. Phase rule diagrams for the systems sodium palmitate: sodium chloride: water,[1] potassium oleate: potassium chloride: water,[2] potassium laurate: potassium chloride: water,[3] have been mapped out, and further, W. J. Elford, working on a semi-technical scale has proved conclusively that the equilibria occurring in a mixture of commerical oils with electrolytes, are exactly similar to those found in the systems of pure chemicals mentioned above.[4]

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[1] McBain and Langdon: J. Chem. Soc., **127**, 852-870 (1925).
[2] McBain and Elford: J. Chem. Soc., **1926**, 421.
[3] McBain and Field: J. Phys. Chem., **30**, 1545 (1926).
[4] See Jerome Alexander's "Colloid Chemistry," Vol. I, Chap. V, by J. W. McBain.

In the light of this new knowledge it was determined to attempt to apply our new method of investigation of saponification to the systems resulting from the addition of sodium chloride to the mixture of oil, soap and aqueous alkali. From Fig. 1 of McBain and Langdon's paper (loc. cit.) we know that the addition of salt in increasing quantity to a homogeneous $0.5N_w$ solution of sodium palmitate at 90° produces no change in the homogeneity of the solution until a concentration of about $1.0N_w$ sodium chloride is reached. The solution then divides spontaneously into two (or possibly three) liquid layers (neat soap and nigre, or neat soap, nigre and lye). A further small increase in the concentration of salt suffices to convert this into two liquid layers, neat soap and lye. Miss Harrington when saponifying pure tripalmitin in presence of sodium palmitate and sodium chloride in this laboratory (see Table VI), chose her concentrations of salt so that the first and the third types of equilibria were represented. Her experiments were carried out in duplicate and the general form of the curve is that shown in Fig. 3. With the soap in homogeneous solution the rate constant is greatly increased by addition of salt. When sufficient salt has been added to produce neat soap: lye k is halved, but rapidly regains a higher value even within the neat soap: lye region.

The curve with coconut oil and coconut soap (Fig. 3) is the results of a more extensive series of experiments carried out by one of us (M. T.). Here again by utilising the unpublished diagram of W. J. Elford for coconut oil soap and sodium chloride it was possible to choose concentrations of salt which produced equilibria corresponding to those existing in the solutions of sodium palmitate: sodium chloride: water studied. With this oil also the rate constant increases while the soap and salt are in homogeneous solution and drops as soon as liquid layers are formed. Further addition of salt again increases the rate constant to above its previous maximum value and the high rate is maintained when the soap is grained out and the sodium chloride is added up to saturation.

The general conclusions to be drawn from the results so far obtained are reserved for a subsequent communication dealing with experiments in more concentrated solution.

Summary

1. A rapid and convenient method has been developed for the measurement of rate of saponification of oils by aqueous alkali whereby the influence of each factor can be isolated and measured independently. A very simple graphical method suffices to integrate the results.

2. The rate is in all cases proportional to the concentration of hydroxyl ions as measured by the hydrogen electrode.

3. The first small amount of oil greatly enhances the rate, probably because it is all emulsified, whereas further additions have a relatively slight effect.

4. The rate is more than proportional to the amount of soap in solution.

5. The effect of salt depends upon the physical state of the system but the fastest rates have been observed in presence of concentrations of sodium chloride approaching saturation.

6. Addition of glycerine slightly diminishes the rate.

7. Under comparable conditions tripalmitin is more rapidly saponified than coconut oil, in agreement with 3 and 4 above.

Department of Physical Chemistry,
The University,
Bristol, England.
October 16, 1926.

NEW BOOKS

International Critical Tables. *Edited by E. W. Washburn. Vol. I. 28 × 22 cm; pp. xx + 415. New York and London: McGraw-Hill Book Company, 1926. Price: $12.00.*

"At the organization meeting of the International Union of Pure and Applied Chemistry, held in London in June 1919, the Union approved as one of its projects the compilation of International Critical Tables of Numerical Data of Physics, Chemistry, and Technology, and assigned to the United States of America the financial and editorial responsibility for the undertaking. The project was later given the patronage of the International Research Council at its Brussels meeting in 1923.

"On behalf of the National Academy of Sciences, the National Research Council of the United States accepted the executive, editorial and financial responsibilities of the project, and with the cooperation of the American Chemical Society and the American Physical Society, created a Board of Trustees to take charge of the financial and business administration, and a Board of Editors to supervise and carry out the preparation of the text.

"The first action of the Board of Editors, early in 1922, was to approve the appointment of Corresponding Editors in different parts of the world, particularly in all those countries in which conditions were such that they might be expected to take a really active part in the undertaking. In making these appointments, the Board first sought the advice of competent individuals in the several countries, and in accordance with the suggestions thus received, appointed ten Corresponding Editors and empowered them to arrange for Advisory Committees to assist in the work. In the case of certain countries, the Board was unsuccessful in its efforts to secure cooperation, usually either because of the receipt of no reply or an unfavorable reply, or through failure of the Corresponding Editor, after appointment, to perform his duties.

"The general plan of preparation of the Tables was as follows: The subject matter was first divided into some 300 different sections. The Corresponding Editors were then asked to recommend for the several sections one or more persons who should either have some special knowledge of the subject matter of the section, or be otherwise qualified to pass critical judgment upon the available information on the subject. On the basis of the recommendations thus received, the Board of Editors selected the Cooperating Experts, to whom was intrusted the task of critically compiling, and displaying in suitable form, the available quantitative information upon the several topics. In making these selections, the Board consistently endeavored to secure the best man *available* in the light of all the information which it possessed. In certain special fields composed of closely related topics, the Board provided also for the appointment of Special Editors to supervise the work and to assist in the final arrangement of the material."

In the first volume the material is presented under the general headings: national and local systems of weights and measures; symbols, basic constants, conversion data, dimensions, definitions; chemical elements and atoms; thermometry; laboratory methods for producing and maintaining constant temperatures; laboratory methods for maintaining constant humidity; barometry and manometry; psychrometry, density of moist air, change in barometric pressure with altitude; volume of liquid menisci; weights and weighing, calibration of volumetric vessels; standard buffer solutions and acid-base indicators; high vacuum technique; errors of observation; physical properties of chemical substances (including ready reference tables, crystal structure, disperse systems, sweetening agents, odoriferous agents); radioactivity; astronomical and geodetic data (including stars and nebulae, time, the solar system, composition of the atmosphere, the earth, gravity data); aerodynamics.

The ground covered is very much more extensive than that in Landolt and Börnstein's Tables; but the great merit of this work is that the data are to be presented critically, so that one at least knows which figure the sub-editor of any particular table considers the best. Of course, the sub-editor may be wrong; but he is better qualified to judge than all except a very few of the readers. Few things are more trying to the scientific man who is

not an expert, let us say on densities, than to find several widely differing densities for a given substance in Landolt and Börnstein, with nothing, except perhaps the date, to show which is probably the best.

It is a stupendous task which Dr. Washburn and his associates have undertaken because there are to be six of the volumes. So far as the reviewer is qualified to speak, this first volume is a great success and reflects credit on everybody connected with the work. It is a pleasure to learn that the advance subscriptions have exceeded all estimates. The scientific and technical public is more intelligent than we dared think.

Wilder D. Bancroft

Molybdenum, Cerium and Related Alloy Steels. *By H. W. Gillett and E. L. Mack. 23 × 16 cm; pp. 299. New York: Chemical Catolog Company, 1925. Price: $4.00.* "This book is based on the thesis that a given alloy steel is a member of a class rather than a special entity and that with due regard to required heat-treatment it is often possible to produce, by combination or substitution of alloying elements, several chemically different steels which are practically interchangeable for the same engineering application.

"This idea has guided many metallurgists in recent years and has been emphasized well by Aitchison in his "Engineering Steels." Aitchison, however, has confined that book to the alloy steels universally available to the engineer. American conditions make it desirable that molybdenum steel also be discussed from this point of view. The United States has large reserve supplies of molybdenum while the domestic supply of many of the other alloying elements is restricted, either by Nature or by economic conditions. Molybdenum is now known to be one of the most potent alloying elements for steel. American steel makers know how to make molybdenum steel, and have made it readily obtainable in the American market.

"Molybdenum is destined to take its place beside nickel, chromium and vanadium as an alloying element. Before it can take and hold that place, its possibilities and limitations must be better understood, and it is for this better understanding that this book is written. The largest gaps in the knowledge of molybdenum steel seem to be its effect on the endurance and impact properties, and its effort on the properties of 'transverse' specimens. The experimental work herein recorded was planned with a view to filling those gaps. Since the experimental work on both molybdenum and cerium was carried on together, the title has been chosen to express this fact at the risk of erroneously seeming to class cerium as necessarily a true or a useful alloying element."

The chapters are entitled: the effect of alloying metals as a class; effect of alloying metals as individuals; interchangeability of alloying elements; molybdenum and cerium as alloying elements; the effect of molybdenum as shown by the transition points; importance of dynamic tests; tensile and impact test data for molybdenum and cerium steels; endurance tests of heat-treated molybdenum and cerium steels; normalized molybdenum steels; tests of longitudinal and transverse specimens; molybdenum, cerium, and zirconium in nickel-silicon steels; summary of the effect of molybdenum and cerium as alloying elements in steel.

"Pure iron is soft and ductile. It is classed with steel because of its chemistry rather than its strength. If no combination with iron were possible, the ferrous alloys would not have their dominant position and our minds would not make the automatic distinction between ferrous alloys as rather hard and rather strong, and non-ferrous as rather soft and weak. The addition of carbon to iron gives steel, a malleable alloy of iron and iron carbide," p. 17.

"An alloy steel is, broadly, one in which properties not attainable, or attainable with difficulty, in carbon steel are secured, or secured more readily by the addition of some other element or elements. The alloying elements strengthen the steel," p. 18.

"The comparison of alloy steels is made complex by the fact that no single property tells the whole story. Among steels similarly handled, *i. e.*, by rolling and normalizing, by annealing, or by quenching and tempering, strength and ductility are inversely connected the stronger steels being the more brittle and the weaker the more ductile. In some cases, the maximum strength is the property more desired.

"When great ability to resist static distortion is required, the proportional limit is the property of greatest interest. When a machine part must resist repeated stress, the endurance limit is the most important one. If the design of the part calls for sharp changes of section or notches, like a screw thread, and the part may be subject to sudden blows, the ability to withstand impact is of importance.

"Some of these properties are inter-related, but seldom by straight-line relations. In going from the hard to the soft state in a given steel, the ductility and the resistance to impact increase more readily on the soft end of the curve; but on the very hard end, say above 200,000 pounds per square inch tensile strength, these properties may increase instead of continuing to decrease," p. 18.

"The latitude in heat-treatment conferred by alloy elements applies not only to the quenching or hardening operation, but to the tempering or softening operation as well. Alloy steels as a class resist tempering more than do the carbon steels. Not only do the former tend to harden more completely, but, if equally hardened specimens of the two classes are compared we find that the same draw temperature gives a softer and weaker product with the carbon steel than with the alloy steel.

"The resistance to tempering is usually great in those alloy steels, which show the greatest propensity toward hardening. While there may be no direct connection between the two phenomena, it nevertheless frequently happens that the steels containing enough of suitable alloying elements to make the austenite sluggish in breaking down into martensite are also sluggish in decomposing to secondary troostite and sorbite, and the sorbite especially is reluctant to soften further.

"According to Scott, silicon and chromium tend to make martensite delay its transformation to secondary troosite until higher temperatures are reached, as shown by heating of the hardened steels, while the other alloying elements do not change the transformation temperature. The troostite-sorbite change and the stages in the coarsening of sorbite cannot be followed by heating curves.

"This sluggishness towards tempering allows a good many alloy steels to be drawn for long times at relatively high temperatures without softening the steel unduly. But it is generally accepted that the release of internal stresses, set up in quenching, increases with increase in draw temperature as well as with time at a given temperature. Alloy steels may thus be made much freer from internal stress than carbon steels of equivalent physical properties.

"Not all the elements used for alloying with steel exert all the effects above noted, and the percentage of the various elements required to produce a certain result may vary widely. Nevertheless, the benefits conferred by most alloying elements are quite similar in nature, though varying in degree. It gives a very nearly correct view of the alloy steel situation to consider that, by suitable adjustment of the content of carbon, manganese, chromium, nickel, vanadium, molybdenum, etc., we can produce by proper heat-treatment an almost unbroken gradation of mechanical properties and engineering usefulness, ranging from an annealed low-carbon steel on one end to an air-hardened nickel-chromium-molybdenum-vanadium steel on the other. Even high-speed tool steel, though differentiated from the structural and automotive steels by the special carbides present, fits in on the end of the series," p. 26.

"Cerium appears to have no true alloying effect in steel and to do no good. Since it gives rise to inclusions, it probably does harm. There is a possibility that it might be used as a scavenger to eliminate or control sulfur if means could be found to eliminate the accompanying inclusions.

"Molybdenum is a very potent alloying element. Even small amounts greatly increase the propensity of steel toward hardening on quenching. This property is increased in the presence of other hardening elements. That is, molybdenum intensifies the hardening effect of other alloying elements.

"After hardening by quenching, the molybdenum steels require decidedly high draw temperatures to soften them to the same degree as other similar alloy steels. Heat-treated molybdenum steels of a given strength or hardness can therefore be produced by the choice

of a suitable composition of the steel as to molybdenum and other alloying elements, in which, by a long draw at a high temperature, quenching stresses can be largely relieved without softening the steel beyond the desired point. The ductility of the molybdenum steels at a given hardness, tensile strength, or elastic limit, is equal to that of any other and superior to most alloy steels. The great resistance to tempering makes the molybdenum steels attractive for use where strength at high temperatures is desired.

"When a very high tensile strength at ordinary temperatures is sought, molybdenum again offers a ready and certain means of attaining the result desired. For strengths which can be readily obtained by other heat-treated alloy steels, the use of molybdenum appears to allow as great a latitude in forging and quenching temperatures as is safe with any other alloy steels, and greater than is safe with some others.

"If a steel is to be used in the normalized condition, its molybdenum content should preferably be low. Steels in which the addition of molybdenum has produced a strong tendency toward air-hardening do not give very good results in the normalized state, unless a low proportional limit can be tolerated. In general, the molybdenum steels should be heat-treated to develop the best combination of properties.

"When heat-treated molybdenum steels are compared with other alloy steels on the basis of tensile strength or Brinell hardness, their behavior on repeated-impact or single notched-bar tests is the same as that of the others. The endurance properties of molybdenum steels, again compared with other alloy steels on the basis of strength or hardness, are substantially the same as those of other alloy steels.

"If the comparison is made on the basis of the same heat-treatment, especially at the same draw temperature, the molybdenum steels are stronger in endurance test and weaker in shock test; but this is because the molybdenum steels resist tempering more than the other steels and are therefore harder, stronger in tension, and less ductile. At a very high strength and hardness, the endurance properties of amolybdenum steel subjected to a long tempering process at a high temperature will probably be superior to those of other steels (which, in order to get this high strength, may only be tempered at much lower temperatures), because of the better release of quenching stresses. Within the machineable range this advantage is probably slight," p. 226.

"Properties similar to those obtained through the use of molybdenum can be obtained by various combinations of the other alloying elements, with suitable heat-treatment. However, the control of temperature in quenching and drawing, in order to obtain the desired results must, in general, be closer in the absence than in the presence of molybdenum. Uniformity of product will therefore generally be easier to maintain with the commercial molybdenum steels than with other alloy steels of the usual commerical composition.

"When the molybdenum content is very high, or when much molybdenum is added to a steel of the high nickel-chromium class, the control in drawing to a relatively low Brinell hardness would be less easy than without the molybdenum, while in drawing to a spring temper it would be easier. This is because the molybdenum increases the resistance to drawing so that the steel remains hard at high drawing temperatures, but when such a steel finally reaches the temperature at which softening begins, further increase in temperature hastens the softening at a high rate," p. 228.

There are five appendices: (A) composition, rolling, and heat-treatment of the experimental molybdenum and cerium steels; (B) test-pieces and methods of testing used, with special reference to endurance testing; (C) composition, rolling, heat-treatment, and test-pieces of experimental nickel-silicon steels; (D) finding list of references to sources of information on molybdenum steel, arranged according to the composition of the steel; (E) references to the literature.

This is an admirable monograph. *Wilder D. Bancroft*

Introduction to Theoretical Physics. *By Arthur Haas. Vol. II. Translated by T. Verschoyle. 22 × 14 cm; pp. + 414. New York: D. Van Nostrand Company, 1926. Price: $6.00.* The second volume is divided into three parts: atomic theory, theory of heat, and theory of relativity. Under atomic theory the chapters are entitled: the ele-

mentary quanta; theory of the hydrogen atom; Röntgen rays; theory of the elements; general theory of spectra and of atomic structure. Under theory of heat are two chapters, entitled statistics and thermodynamics. Under theory of relativity are also two chapters, entitled special theory of relativity and theory of gravitation.

"The problem of experimental Röntgen spectroscopy consists chiefly in the exact determinations of wave-lengths, both of absorption band heads and of individual emission lines. Much the most accurate method of measurement is the direct one based on Bragg's equation of crystal reflection, but this method can only be applied within a limited region of wave-lengths. The majority of wave-lengths are measured by means of a rock-salt or calcite crystal, which, as already mentioned in an earlier section, can be used for wave-lengths up to about 5,000 X. U. Wave-lengths more than twice as large can be reached with the help of selenite or mica, which have a larger lattice constant. Exact measurements by means of crystals have been perfected, principally by Siegbahn, to such a degree that, at the present time, Röntgen wave-lengths can be determined with an accuracy of about a millionth part of the measured value," p. 137.

"*From the spectrum of the simplest of all atoms, hydrogen, it is clear that an electron* revolving around the atomic nucleus can leave its usual orbit and revolve in an orbit of *higher quantum number. Quite generally, we say that an atom is excited when one of its* electrons describes an orbit other than its normal one, the electron then having a higher *energy than usual.* The excitation of an atom thus always demands an introduction of energy, while, on the return of the atom to its normal state, energy is liberated.

"As subsequent spectroscopic considerations will show, the multiplicity of higher levels, to which the electron can temporarily be raised, is very great. Each of these levels, however, which are not present in the normal atom and can only be realized when the atom is excited, is associated with a quite definite energy value, just as is the normal state. Hence, from amongst the manifold of excited states there must be one state that is distinguished by its having the smallest excess of energy over the normal energy value. This state is termed, in a narrower sense of the word, simply the excited state, and its surplus energy is called the excitation energy of the atom. It therefore represents the smallest quantity of energy which a normal atom of the element concerned can ever take up in connection with a change of its internal energy.

"The excitation of atoms is, of course, most readily effected with the most loosely bound electrons. These are obviously the peripheral electrons, which an atom loses when it enters into chemical combination as a positive ion, and which are therefore called the valency electrons. Since the elements in the first group of the periodic system are positively univalent, those in the second vertical column positively divalent, and so on, we must assume that the atoms of the elements in the first group each possess a single valency electron, those in the second group two valency electrons each, and so on.

"*In general, changes in the orbit of the peripheral valency electron are probably responsible for those variations of the internal atomic energy which, in accordance with Bohr's frequency condition, manifest themselves in the optical spectra. For, in the optical* region, a light-quantum is roughly a thousand times smaller than in the region of Röntgen rays so that optical lines can only be due to those electrons for which, because they are loosely bound, a change of orbit can be effected by a relatively small expenditure of energy. Moreover, it is easy to understand why the excitation of an atom should, in general, find expression only in the peripheral electrons, because it is only these electrons that, since they describe the highest-quantum orbits in the normal atom, will, on a transition to an orbit of still higher quantum number, find it unoccupied. An inner electron, on the other hand, must, on a transition to a higher-quantum orbit, generally find it already completely occupied (as follows from concepts of the grouping of electrons, to be discussed in greater detail later).

"We must assume that an excited state of the atom is not only abnormal, but also extremely unstable. After a very short sojourn, which we shall later find to be of the order of 10^{-8} sec., the return to the normal state takes place. Furthermore, provided the surplus energy is not changed into kinetic energy, this return is accompanied by the emission of a

light-quantum whose frequency, according to Bohr's condition, is equal to the quotient of the energy released and the elementary quantum of action. If the atom was not in the lowest of the excited states, but in one more highly excited, the return to the normal state may, of course, follow by steps, so that the emission spectrum then produced will contain lines for which both the initial and the final levels are possible only in an excited state.

"Conversely, the excitation of an atom, or its transformation from an already excited to a more highly excited state, can also be effected by the absorption of a light-quantum, provided the product of the frequency of the light-quantum and the elementary quantum of action be equal to the difference in energy between the actually existing and a higher-quantum state.

"A far more frequent way of exciting atoms than by absorption, however, is by supplying the requisite energy from the heat store of the body concerned. According to the fundamental concept of the kinetic theory of heat, incessant collisions occur in a gas between the rapidly moving molecules. By virtue of these collisions, energy of translation can of course be changed into intra-atomic energy, but when the atom struck was previously in the normal state, this can only happen if the relative kinetic is at least as large as the excitation energy. (In the monatomic vapours of the metals in the first two groups, which have been chiefly investigated, as well as in the rare gases, the concepts of atom and molecule are synonymous.) Now, when atoms thus excited by collision return to the normal state with the emission of light-quanta, the well-known phenomenon of thermoluminescence is observed. Moreover, the atoms of a gas can be excited, not only by sufficient heating, but also by collisions with rapidly moving ions in electrical fields, as is shown by the luminescence of rarefied gases in Geissler tubes," p. 146.

"Theory teaches us to expect that, when any vapour commences to glow with rising temperature, the first spectral line to be observed will be that corresponding to the transition from the lowest excited state to the normal state. The longer the wave-length of this line, the smaller will be the excitation energy, and the lower the temperature at which emission of the line will begin. As this temperature is exceeded, we must further expect that the transfer of translational energy will be sufficient to produce higher and higher excitations, so that new spectral lines will be continually appearing. In point of fact, all these theoretical conclusions are confirmed by experiment," p. 149.

"The easiest spark spectra to produce are those of the second group elements, a temperature of 2,000°C. being sufficient for this purpose, for their simple ions still contain one loosely bound electron. Arc and spark spectra of these elements are thus often to be observed together. On the other hand, it is extremely difficult to generate the spark spectra of the alkali metals, since their atoms in the neutral state only contain a single valency electron.

"These conclusions from Bohr's theory of the atom provide an explanation of several apparently paradoxical results in solar spectroscopy, as was first pointed out in 1920 by the Indian physicist, Saha. It had previously been quite inexplicable why sodium should appear very strongly in the solar spectrum, whereas potassium appears only weakly, and rubidium and caesium are entirely absent. According to Saha's striking explanation, the alkalii metals are present in the sun, just as in the earth. To some extent, however, they remain unnoticeable, because, in consequence of the high temperature, they are almost invariably ionized, and their spark spectra, the lines of which lie in the ultra-violet, escape spectroscopic observation. That the arc lines of Na occur strongly in the solar spectrum, those of K only weakly, and those of Rb and Cs not at all, follows from the fact that Rb and Cs have the smallest ionization energies, K having a somewhat higher, and Na a considerably larger value. In contrast to the alkali metals, the alkaline earths are represented in the visible portion of the solar spectrum by the lines of their ionized atoms as well; for instance, the strong Fraunhofer lines *H* and *K* both belong to the spark spectrum of calcium.

"Moreover, Saha found in Bohr's theory a simple explanation for the remarkable fact that the heavier element calcium is to be observed in the spectrum of the sun's atmosphere at much greater heights than the much lighter element hydrogen. For the calcium lines lying in the visible region of wave-lengths require a smaller excitation energy than the

hydrogen lines lying in the same region; the hydrogen lines which are readily excited belong to the ultra-violet. In the higher regions of the sun's atmosphere, where the temperature is less than in the lower regions, the energy transferred by molecular collisions therefore suffices to excite the visible calcium lines, but not the visible hydrogen lines," p. 151.

"The radiation emitted by a body whose atoms are excited by primary rays is called fluorescent radiation. In the special case in which the wave-lengths of the secondary and the primary radiation are identical, we speak of a resonance radiation. According to the discussion in a previous section, we may expect to meet with such radiation when light of the wave-length of a resonance line of an element passes through the vapour of the element at a temperature below that at which any of the atoms are excited.

"The phenomenon of resonance radiation was discovered and investigated long before the atomic theory was established, first by Wood in the case of *mercury*, and subsequently by Dunoyer, Wood, and Strutt in the case of alkali metal vapours, especially sodium vapour. At low pressures, the total energy of the re-emittted light does, in fact, agree with the energy absorbed from the primary radiation. It is only when the pressure is increased that a part of the absorbed primary radiation is changed into molecular energy of translation, with a resulting heating of the fluorescent vapour.

"When a gas is irradiated with light of a frequency greater than the resonance frequency and corresponding to the difference in energy between the normal state and a higher, excited state, the return of the atom from this more highly excited state may take place in steps. In the fluorescent radiation, therefore, lines of greater wave-length than that of the exciting light may occur. Under no circumstances, however, can an atom which, before excitation, is in the normal state, emit fluorescent radiation of shorter wave-length than the primary radiation, and in this lies the explanation of Stokes's rule of fluorescence, which was mentioned in an earlier section. Only when the irradiated atom has been previously excited can it happen, by way of exception (*e. g.*, on a return to the normal state), that the wave-length of the fluorescent radiation may be shorter than that of the exciting radiation," p. 176.

"For many elements, it has been possible to make direct experimental determinations of the excitation potential by purely electrical methods. Using suitable apparatus, the electrons are made to pass through the gas or vapour, and the resulting current is measured with a galvanometer, while the applied potential difference is also observed. If the current be plotted on a graph against the potential, the curve exhibits a strongly marked discontinuity for the potential at which inelastic impacts first occur. With many elements, the first flashing out of the resonance line caused by the electronic collisions could be observed at this potential, and this in itself must be regarded as a brilliant experimental confirmation of Bohr's frequency condition.

"From the point of view of Bohr's theory, further discontinuities in the current are to be expected for values of the potential which, when multiplied by the elementary quantum of electricity, give the energy difference between the fundamental state and a state excited to a higher degree. The determination of these closely adjacent potential values, however, generally meets with experimental difficulties, and has hitherto only been successful in the case of mercury. On the other hand, the potential at which the electron impacts first produce ionization of the atoms of the gas can be fairly sharply determined for many elements. This potential is called the ionization potential. It must be equivalent to the fundamental term of the atom, inasmuch as this corresponds to the work necessary for the removal of the electron concerned from the atom. The ionization potential must therefore satisfy eqn. (1) for a wave-length corresponding to the fundamental term," p. 181.

"Like the phenomena of fluorescence, photochemical reactions can also be "sensitized." That is to say, under certain circumstances the reactions can also be produced by light of wave-lengths which are not absorbed by the reacting molecules, provided only that a sensitizer which can absorb the light be added. Owing, presumably, to molecular collisions, the surplus energy absorbed is transferred from this sensitizer to the molecules of the substances concerned, which can then react. This appears especially clearly from an experiment of Franck and Cario, in which mercury vapour served as sensitizer for the dissociation

of hydrogen. It is known from thermochemical measurements that the energy required for the resolution of a molecule of hydrogen into its two atoms amounts to about 6×10^{-12} ergs. Dividing this by the elementary quantum of action, we obtain, a frequency of about 9×10^{14} sec.$^{-1}$, or a wave-length of approximately 3,000 Å.U. A non-excited hydrogen atom, however, cannot absorb any radiation of greater wave-length than its resonance line, which (as the first line of the Lyman series) lies at 1,216 Å.U., far in the ultra-violet. Franck and Cario introduced mercury vapour into the hydrogen, and submitted the mixture at sufficiently low temperature to the action of the rays of 2,537 Å.U. wave-length emitted by a quartz mercury lamp. *Although, in accordance with what we have just said,* these rays could not be absorbed by the hydrogen, yet a dissociation of the hydrogen took place. This was clearly proved by a reduction of metallic oxides which, as is known from experience, can only be effected at the temperature in question by monatomic, but not by diatomic, hydrogen. For the rest, the best-known instance of a photochemical sensitization is afforded by the sensitization of a photographic plate with suitable dyes which possess in the red the absorption lines lacking, in that region, in the silver halides.

"The converse of photochemical processes is represented by chemico-luminescence, due to a transformation of chemical energy into light-quanta. A well-known example of this is the oxidation of aldehydes at low temperatures, which is accompanied by an intensive luminescence. Haber and Zisch have shown that, on leading a stream of chlorine through sodium vapour, chemico-luminescence ensues; it can be recognized by the appearance of the characteristic D-lines of sodium at a temperature at which a luminescence due to heat is obviously excluded.

"Chemical reactions may be produced not only by the absorption of light-quanta, but also by electron collisions. The experimental investigation of these processes promises to be of great importance, because it permits of an exact determination of the minimum energy requisite for the initiation of a chemical reaction," p. 191.

"In the light of modern atomic theory, Dulong and Petit's Law appears simply as a special case of a more general expression for the atomic heat, which is approximately represented by eqn. (3). This equation was derived in 1907 by Einstein, and formed the first application of the quantum principle to mechanical oscillations. Exact determinations carried out by Nernst and other investigators subsequently to the formulation of Einstein's law have shown, in fact, that the atomic heats of all substances converge at sufficiently high temperatures towards 3R and, at sufficiently low temperatures towards zero. The atomic heat of diamond (C_v) at about 1,000°C. amounts to 5.5 cal. On the other hand, the atomic heat of copper, for example, falls to 3.38 at 88° K., to 0.54 at 33° K., and to 0.22 cal at 23° K. The decrease is certainly most marked with diamond. At 86° K. the atomic heat is but 0.03 cal., and at 23° K. it was found by measurement to be 0.00 cal.; *i. e.*, at these low temperatures the idea of temperature is practically meaningless in the case of diamond," p. 281.

The student will have difficulty with the discussion of the theory of gravitation. It is perfectly true that we shall get the same apparent effect with an observer moving at a constant rate and a particle undergoing uniform acceleration or with an observer undergoing uniform acceleration and a particle moving at a constant rate; but that merely indicates that there are two ways of considering a homogeneous gravitational field, p. 336. The important thing is the calculation made by Einstein. This is given on p. 370; but not in a form or with an emphasis which will overcome the false impression produced by the preceding pages. For pedagogical effect, a reference to it should have been made on p. 337.

Wilder D. Bancroft

Chemistry in the World's Work. *By Harrison E. Howe. 22 × 15 cm; pp. vii × 244. New York: D. Van Nostrand Company, 1926. Price: $3.00.* "The object of this work is to emphasize, in language easily understood by those not technically trained, the part which chemistry has played in assisting in the attainment of our present level of civilization." The chapters are entitled: solitude; mental isolation; allies of the sun; food and famine; contributions of chemistry to cloth and clothing; decoration—escape from monotony;

metals, the master; materials of construction; permanency of possessions; health and sanitation; power; abolition of drudgery; chemistry in national defense; chemistry, a tool; analysis and synthesis; the trend and purpose of modern research.

The following quotations will give some idea of the scope and quality of the work. "Chemistry has also contributed to the safety of transportation. The materials supplying the light in the lighthouses are made under chemical control. The powerful lenses also come from the chemist's workshop, and the small gas buoys are his product. An interesting example is the red lens universally used as a danger signal on railways. Before the chemist had shown how to make a glass which is called spectroscopic red, the lenses having a red appearance did not always transmit a red light. By the use of selenium and some other materials it was shown that a glass could be made which would always transmit red light even when submitted to a severe spectroscopic test. Previously there had been cases where engineers undergoing a periodic test for color blindness might, due to some imperfection of the sight, see from the same lens red and green alternately, depending upon the distance they chanced to be from the light. With a spectroscopic red lens, we may be sure that red light will be transmitted, and if any other color is reported to be seen, we may be sure the fault lies wholly with the observer and not with the lens," p. 6.

"Casinghead gas is that which accumulates in the petroleum wells and at one time was allowed to waste. This is now condensed, blended, and made available by the hundreds of millions of gallons. Then a chemist found that one essential difference between natural gases was the percentage of wet gas later identified as something recoverable as gasoline. Those vapors are collected in oil from which the gasoline is distilled, or, since our wartime defense against poisonous gases has taught us so much of activated charcoal, this form of carbon is used as an absorbent for these gasoline vapors," p. 11.

"No balloon fabric has yet been found through which air will not diffuse, thus diluting the gas and diminishing its lifting power. Pure gas has a considerably greater lifting power than gas mixed with air. Hydrogen, though cheap to make, cannot be purified following contamination due to air leaking into the gas bags. It is therefore changed some fifteen times a year. Helium can be purified at low cost and re-used. This constitutes an advantage which greatly offsets any original difference in the first cost of the two gases. Indeed, the net cost of helium under the most modern conditions of operation and purification is no greater than hydrogen," p. 19.

"A stone cast into still water gives rise to a series of ripples most pronounced near where the stone struck and fading away as the distance from this point increases. If stone after stone could be thrown in exactly the same spot, ripples of a given magnitude might be maintained and the finer ones might even reach an increased distance from the center. If there were some way of introducing more energy into the feeble waves distant from the center, these outermost waves might be increased in size to compare with those near the source of the impulse. Roughly speaking, what has been done in long distance telephony is to supply energy to these waves, that they may be kept at the strength of the initial impulse. This method of attacking the long distance problem made every instrument a long distance telephone, and even the rural telephone is found unsatisfactory only when all the other subscribers on the party line insist on taking down the receivers when they hear a call, that nothing in the way of news or gossip may escape them. This practice diverts so much energy that the original parties to the conversation have an insufficient supply left them," p. 31.

"A variety of chemical compounds have been used in sound-reproducing devices; but the most rugged, permanent, and withal satisfactory record has been of the synthetic resin type. It has been the chemist's major contribution to this art," p. 35.

"To-day, acetylene is so universally available in compressed form, another chemical achievement, that there seems no need for any difficulty in its production and use. Just as the mariner is often protected by the flashes of acetylene gas in the gas buoy off shore, so also is the motorist warned on the country highway and in the cities of crossings or danger ahead. A gas accumulator, using acetylene, is the active principle of these highway lighthouses, which flash their warning at regular intervals," p. 47.

"The chemist has helped the animal husbandman to establish important facts with relation to stock feeding. It has been shown that the calcium so important in our diet and largely derived from milk is taken from the skeleton of the cow; hence our interest in learning how to make available through the diet other calcium to keep the animal in healthy condition. The race horses of Kentucky are noted the world over and the blue grass of Kentucky contains a larger quantity of available calcium to strengthen the skeleton of the horse than is commonly found elsewhere. Chemistry has also helped to establish some important economic facts in animal feeding, for it has been shown that there comes a time when a steer literally eats his head off, for without change in feed he proceeds to replace with water a part of the fat previously accumulated at no little expense to its owner. Just as traces of elements are important in the soil, so also they are important in animal metabolism, though the full story is not yet known. The chemist has helped to make a promising start on the chemistry of the ductless glands, and the active principles of some of these have already been synthesized. Enthusiasts predict that with a more complete knowledge of the chemistry of these glands will come the ability not only to control growth, but in the case of the human being to influence mental development as well and perhaps control sex. Indeed, if the prediction of these workers should come true, the power conferred through this work might be greater than the race could properly administer," p. 62.

"A chemical study of the diet of various tribes and peoples serves to explain conditions otherwise mysterious, and if the prejudices and fastidiousness of some peoples can be overcome, this information should be helpful in planning a rational, economical diet. Many have pitied the oriental with his monotonous diet of fish, soya or mong beans, and rice; yet the laborer of the Orient performs a prodigious amount of work on a diet which seems starvation rations to the occidental. One difference has been found to lie in the soya or mong bean as compared with the American Navy bean. The former in the digestive tract produces the types of amino acids of the greatest help to the body, while the Navy bean does not," p. 65.

"How fortunate is the closer cooperation between chemistry and medicine may be emphasized by the delays which accompanied the adoption by the physician of some of the earlier contributions of chemistry. Ether was not recognized as an anaesthetic until 1846, though the compound had been discovered more than five hundred years before, and in that interval unnumbered thousands suffered agony because its ability to produce insensitiveness to pain was not known. Two hundred years elapsed after the discovery of magnesium sulphate by the chemist before the physician learned that it would give great relief in the case of burns, strychnine poisoning, and lockjaw. These are but two of many such instances not likely to recur under modern conditions," p. 147.

"Calcium has also been found indispensable both in the metabolism of man and the domestic animals, and the problem here seems to be how effectively to introduce calcium and have it assimilated. One specialist in hay fever and similar ailments maintains that those having a deficiency of calcium in the blood are the greatest sufferers and adds to his credit cases of relief following the injection of soluble calcium salts into the blood stream," p. 155.

"Sewage disposal has a direct relation to water supply, since improperly treated sewage of one town or of one house may contaminate the water supply of its neighbor. Filtration, sedimentation, and the activity of one or another type of bacteria are usually depended upon to render sewage effluent innocuous. Filter beds from which the sediment may be collected for further disposal are often used. The Imhoff tank has many installations, and of late years the importance of activated sludge, a process where the work of the bacteria is furthered by stirring the sludge with air currents, has won its adherents. Occasionally the plan adopted makes necessary a filtration of the treated sewage, and, as the engineers of the Milwaukee sewage disposal plant found out, this may involve chemistry. It was only after local chemists showed that the hydrogen ion concentration must be adjusted and the temperature controlled that it was found possible to filter the sludge at all, and but for the application of this knowledge an elaborately designed and expensive plant might have failed of its purpose," p. 160.

"At least one plant in the United States is giving a thorough test to the mercury boiler, a plan which seeks to take advantage not only of the greater heat which the mercury vapor can carry, but the use of the superheated vapor in a turbine, after which the heat is given up to water for the formation of steam, the combined steps giving a much increased return for the fuel consumed. Experiments have also been conducted with diphenyl ether and with sulfur dioxide as the medium along the same lines," p. 176.

"Dr. W. R. Whitney, in his Los Angeles address before the American Chemical Society, said that if all the electrons, now believed to be the ultimate particles of matter, in a drop of water could be enlarged until each of them became as big as the original drop of water they would form a layer three feet deep entirely covering the earth. The molecules are so small that if a glass of water were thoroughly stirred with all the water in the earth and in the sea, and a second glass filled with a mixture, it would contain two thousand of the original molecules," p. 220.

"Our day is unique in the extent to which scientists are cultivating the borderlands between the major divisions of science. Excellent and well known examples are to be found in geophysics, astrophysics, and biophysics. Physical chemistry developed rapidly as a specialty and has grown in importance until it bids fair to dominate the entire chemical field. Its laws and theories are being everywhere applied. Methods peculiar to physical chemistry find a place in all research laboratories, and many of our most remarkable recent achievements in industry must be credited to men well grounded in its principles. Biochemistry affords opportunities unsurpassed by any science and worthy of any genius, dealing as it does with the most complex substances; the problem is further complicated in that reactions must be interpreted almost in terms of life itself," p. 225.

It is quite remarkable that the author should be able to write such a book as this in his stride, as it were. This had to be done in odd moments and not many of them.

Wilder D. Bancroft

Physikalische Chemie der Zelle und Gewebe. *By Rudolf Höber. Sixth edition. 23 × 16 cm; pp. xvi* × 955. *Leipzig: Wilhelm Engelman, 1926. Price: 39 marks paper; 42 marks bound.* The fifth edition was reviewed a few years ago (**27**, 692; **28**, 1331). There are many interesting things in the new edition. It is now believed that the high concentrations of sodium urate are due to supersaturation and not to a colloidal solution, p. 67. In an acidified albumin solution which has a pH of 2.49 as determined by the hydrogen electrode, methyl violet gives an apparent value of 2.53, which is not bad; but the pH as determined by means of Congo red is 5.30, p. 91. On p. 135 is the statement that equal weights of palladium foil, sponge, and black take up equal volumes of hydrogen, from which Höber deduces that the hydrogen is in true solution. The figures, as the reviewer knows them are that palladium foil takes up about 900 volumes of hydrogen and colloidal palladium about 3000.

Höber points out, p. 145, that an acid dye is taken up by wool more strongly from an acid solution than from an alkaline solution, while the reverse is true of basic dyes. He is also clear that sodium sulphate will tend to strip an acid dye from wool and will tend to force a basic dye on wool; he has not mastered the theory of substantive dyes. He quotes Svedberg, p. 167, to the effect that when colloidal ferric oxide is made finer and finer, the color approaches more and more that of a solution of ferric oxide. It does not do this at all, a very fine suspension of ferric oxide being practically as colorless as water. Höber does not explain how sodium oleate carries haemoglobin through an ultra-filter, p. 171; but it seems probable that this is a case of peptization. The author has apparently not heard of McBain's theory of the colloidal ion or micelle and consequently he has some trouble with Congo pure blue, p. 212, and with the sodium salt of thymonucleic acid, p. 213.

Gelatine is more readily precipitated by alcohol when a mixture of sodium and calcium chlorides are present, than when either of these two salts is present by itself, p. 240. Höber considers, p. 242, that we get the most marked antagonism between ions when the colloid is on the dividing line between a suspension colloid and a hydrophile colloid. On p. 249 the author says that the solubility of difficulty soluble calcium salts (such as calcium sulphate, phosphate, and carbonate) is increased very much by gelatine and enormously by serum.

In the next line it appears that he means the concentration of the suspended material and not the solubility. On p. 250 we learn that sodium chloride diffuses faster in a gelatine jelly than sodium bromide while sodium bromide diffuses faster than sodium iodide. This is very important, if true, and should be checked.

The rate at which camphocarbonic acid decomposes into camphor and carbon dioxide varies in the ratio of 1:15 as one passes from water to aniline as solvent, p. 277. These solvents can be considered as catalytic agents. In laevo-rotary nicotine as solvent the dextro-rotary camphoric acid decomposes more rapidly than the laevo-rotary acid. The author does not agree with Armstrong's formulation, p. 283, that an enzyme builds up the biose which it cannot decompose and decomposes the biose which it cannot build up.

On p. 294 the author calls attention to the well-known facts that stannic chloride and ferric chloride cause exclusively chlorine substitution with benzene, while light causes exclusively addition of chlorine, and iodine monochloride comes in between. He compares this with copper splitting isobutyl alcohol into the corresponding aldehyde and hydrogen, while alumina causes decomposition into isobutylene and water. This again is paralleled by the different actions of pepsin and trypsin on albumin. While Rosenthal succeeded in decomposing starch with frequencies of 440-480 and albumin with frequencies of 320-360, p. 297, the author refuses to accept Rosenthal's hypothesis that enzymes act by setting up definite frequencies.

Very interesting is the observation, p. 305, that the rate of oxidation of oxalic acid in presence of charcoal decreases with increasing concentration of oxalic acid, because the oxalic acid decreases the adsorption of oxygen so much. In some cases involving enzymes, p. 320, the relative reaction velocity is smaller the higher the initial concentration.

Human blood freezes at −0.56° to −0.58°. The blood of all the other mammals freezes at −0.58°, which corresponds, at the normal body temperature, to an osmotic pressure of about eight atmospheres, p. 334. The constancy of the freezing-point is regulated by the kidneys since the osmotic pressure of the urine may easily vary between twelve and twenty-six atmospheres in the course of twenty-four hours. The physiological saline solution for mammals is one percent sodium chloride. The 0.6 percent one is right for frogs which have an osmotic pressure of only four to five atmospheres in the blood, p. 336.

As an instance of indicator errors due to adsorption, Höber cites the case of living muscles p. 381, which were put in a buffer solution of pH = 7.82 and in one of pH = 5.2. The first buffer solution is colored blue by bromthymol blue and the second yellow; but, in both cases, the muscles were colored yellow on additions of crystals of the indicator. Sea water is apparently more alkaline than the blood, p. 383; but there is some question whether the body liquid of sea organisms has exactly the same acidity as the water itself.

Jacques Loeb was able to produce parthenogenetic development by means of hypertonic sea water at Wood's Hole, p. 384, while the experiment failed in California. The reason for this was found to be a difference of alkalinity between the waters of the Atlantic and Pacific Oceans at the two laboratories. The experiments succeeded when 0.0002 mols NaOH was added per liter to the California sea water. Living cherries and red beets do not color water; but if they are killed by heat, the dye is said to come out, p. 403. Höber assumes that this is not a rupture of the cells due to the heating; but is a permanent change in the permeability of the cell membrane. If this is true, it should be possible to produce the same change by suitable additions to the water and it is very desirable that this should be tried. It might easily be possible that one could show reversible permeability with the living beet in this way.

"Some pollens explode and scatter their contents when placed in water because the cell wall cannot withstand the great osmotic pressure. This pressure phenomenon can be shown in a striking way by growing fungi such as *Aspergillus niger* or *Penicillium glaucum* in a concentrated potassium nitrate solution. The cell content increases gradually up to an osmotic pressure of over two hundred atmospheres. If these modified fungi are then brought into pure water, the cell walls are scattered with great force by the colossal pressure set up," p. 413.

Hamburger's method with blood corpuscles does not give real osmotic pressures because different results are obtained with blood from different animals although there are no such differences in the bloods. What happens is that, for each kind of blood, the outflow of the coloring matter is a function of the osmotic pressure, the different membranes breaking down at different pressures, p. 420. The method is apparently satisfactory for determining isotonic solutions.

Osterhout's data for the cell concentrations of *Valonia* with reference to the outside concentrations are quite extraordinary, p. 454.

	Cl	SO_4	Na	K	Ca
inside	1	1	1	40	1
outside	1	7.1	5.1	1	7

The most natural explanation would be that the ions are not present as such; but that seems to be barred out by the high conductivity. If the cell is permeable to water, as is apparently the case, there must be a specific pumping action going on. This is not impossible because we have this in the case of the frog, whose skin is permeable to water and who would burst if the incoming water were not removed through the kidneys, p. 422. It is also interesting to note "that among men we find blood corpuscles containing no sugar although they are in a plasma containing sugar; in other cases the sugar content inside is larger than outside. In some cases of glycaemia, there is relatively little sugar in the plasma and in other cases there is relatively a good deal in the blood corpuscles," p. 465. Although the freezing-points of the blood of different mammals is fairly constant, the composition varies considerably, the potassium content being high and the sodium content being low for the horse, the pig, and the rabbit, while the reverse is true for the ox, the sheep, the dog, and the cat, p. 474.

In the muscles of the frog there is much more potassium than sodium while the reverse is true for the serum, p. 489. On leaching the muscles with sugar solution, the percentage loss (not the absolute loss) of sodium was much greater than that of sodium. This is explained most easily on the assumption of greater adsorption of potassium than of sodium. The experiments on the conductivity indicate that much of the salt is present in a non-conducting form. The laming of muscles by cane sugar solution is believed by Overton to be due to the extraction of sodium.

By impregnating collodion membranes with definite amounts of lecithin, cholesterin, and castor oil, Thieulin has made them impermeable to inorganic salts but permeable to chloral hydrate, cocaine, the salts of the alkaloids, and weak organic acids, p. 513.

"Loewe studied the distribution of methylene blue between water and chloroform in which lecithin, cephalin, or some other lipoid had been dissolved. At low concentrations the distribution was more in favor of the organic solvent than at higher concentrations. Loewe explained this by assuming that the lipoids were in colloidal solution in the chloroform and the dye was adsorbed on the surfaces of the lipoid particles. Freundlich and Gann proved the correctness of this assumption. They found that the distribution of methylene blue was described very accurately by the adsorption isotherm and they considered that the lipoids carried some water into the chloroform, producing there a disperse phase which adsorbed the methylene blue.

"Chemical factors may also play a part. Freundlich and Gann found that chloroform does not itself dissolve methylene blue and does not after addition of neutral fats. When the fats are somewhat decomposed and therefore contain fatty acids, the chloroform-fats take up methylene blue and other basic dyes but not acid dyes. Nirenstein has shown that addition of an organic base gives to a neutral organic solvent, such as oil, the power of taking up acid dyes," p. 509.

Traube and Kohler have shown that narcotics tend to peptize gelatine and consequently to prevent the setting to a jelly, p. 593. This should be studied to see whether this is a peptization due to adsorption, of whether it is a case of the displacement of the water equilibrium. If it is the latter, one ought to have the same narcotics acting like potassium iodide in other cases.

Höber calls *Fundulus* a fish in one place and a sea anemone in another, which is confusing to the chemist. In addition to the calcium-sodium antagonism, there is also a potassium-sodium antagonism. The poisoning action of potassium chloride is increased by addition of sodium chloride until the ratio of potassium is about 1:10. Further addition of sodium chloride decreases the toxic action until an optimum is reached at a ratio of about 1:17. Further addition of sodium chloride causes an increase in toxicity, which is probably due to the sodium ion, p. 682.

Wilder D. Bancroft

Applied Colloid Chemistry. *By Wilder D. Bancroft. Second edition. 21 × 15 cm; pp. ix + 489. New York: McGraw-Hill Book Company, 1926. Price: $4 00.* "Much water," as the author states, "has flowed through the colloid mill in the last five years," and the record of its flow contained in this new and enlarged edition of the much-prized book by Bancroft, will be greatly welcomed by all those who are familiar with the former edition of the work and by many new readers whom this discussion of Colloid Chemistry will undoubtedly and deservedly attract.

While the general arrangement of the subject matter has been found satisfactory and remains unchanged, the growth of knowledge has led to the subdivision of certain chapters, so that separate chapters are now devoted to chemical reactions in which adsorption plays a part (contact catalysis), the electrical properties of colloids, the stability of colloidal solutions, fog, and smoke; and the book as a whole has been enlarged by over 140 pages, giving a concise, clear and comprehensive survey of the whole field of colloid chemistry.

This is a great work and original in its treatment. Although the book can be opened at any page and read with pleasure and profit, it is not a book for a lazy or relaxed mind. As one reads, all one's faculties must be kept alert, for one is borne forward irresistibly not as a smoothly flowing stream but as by a great and turbulent river, with here and there great rapids where one is buffeted by facts, now on this side, now on that; and sometimes brought up sharply by real or apparent contradictions. Not for a moment, however, is the interest allowed to droop as the author enumerates, example after example, the varied applications of colloid chemical principles in the arts and industries as well as in the home. As one reads one cannot but marvel at the obvious extent of the author's knowledge, his critical and sound judgment, and the ability with which the great wealth of facts is sifted and arranged. As in all really great and original works, the author's personality, genial and compelling, shines through every page, lighting up the facts with rose-hued flashes of humor and infusing them with a strong human interest. See, also, how in discussing the blue of turbid media, the artist comes out in the quotation from Bruce's "Assault on Mount Everest": "the blue haze of the monsoon converts the distant shadows from their crude purple-brown to the most magnificent and sometimes brilliant blue. Once or twice one looked in vain on one's palette for a blue of sufficient brilliance and intensity to reproduce the colour of the shadow twenty or thirty miles away."

With the large number of experimental results to which reference is made the reviewer often desired more tables of numerical data, but the insertion of these would doubtless have disturbed the general flow of the discussion, and since full bibliographical references are given, the data can readily be obtained.

The author, being human, has like other fallible mortals allowed a small number of misprints to remain in the text, but they are easily recognised for what they are. But why does he lapse from the pure latinity of univalent and bivalent to the hybridism of trivalent and tetravalent? Is it not also a mistake to say that "Graham suggested calling them colloids, from the French word for glue"? Graham, in his original paper, certainly does not state the derivation of the term colloid which he introduced, but surely we can be certain that one who in the same communication introduces the term pectous, and gives, in a footnote, the Greek adjective from which he formed it, did not go to French for the origin of the term colloid. The student of colloids, however, will probably regard this matter as one "ganzlicher Wurstigkeit", and rightly see in it the tiny pebble thrown by the reviewer to

cause a ripple on the deep pool of grateful appreciation. With or without the recommendation of the reviewer this book will be read by every one who takes an interest in colloid chemistry and its applications; the reviewer has the task merely of announcing its appearance.

Alex. Findlay

Alcoholic Fermentation. *By Arthur Harden. Third edition. 24 × 17 cm; pp. 194. London and New York: Longmans, Green and Co., 1923. Price: $2.00.* The second edition was reviewed six years ago (25, 264). The order of presentation has been changed a little, the chapter entitled carboxylase now coming immediately after the one on the coenzyme of yeast-juice. There is only one new chapter, the reducing enzyme of yeast.

"That the reducing properties of yeast are certainly due, at all events in large part, to an enzyme was shown by Hahn (1903), who found that yeast-juice reduced methylene blue but lost this property almost entirely when heated. Dried yeast and zymin (yeast treated with acetone) also reduced methylene blue, but more slowly than yeast-juice," p. 79. Yeast and its preparations are now known to bring about a very large number of reductions. "The reductions in all these cases are carried out by adding the substance to be reduced to a fermenting mixture of 10% cane sugar solution and 10% of living yeast, and it is sometimes necessary to add a further amount of yeast and sugar to complete the reduction. Thus the reduction of aldol was effected by gradually adding 50 g. of aldol to a mixture of 250 g. bottom yeast with 25 litres of water and 250 g. cane sugar, two additional amounts of 100 g. yeast and one of 200 g. together with some water being added before the sugar had all disappeared. Two similar fermentations were carried out simultaneously and after 7 days 65 g. of 1.3-butylene glycol were obtained from the 100 g. of aldol used i. e. 63.5% of the theoretically possible amount. This glycol was optically active, $a = +10.9^{\circ}$ (l = 1).

"This particular experiment well illustrates two striking features of these reductions.

1. The yield is frequently more than 50% of the theoretical amount, being in some cases as high as 80%. This affords definite proof that the alcohol is not produced from the aldehyde by Cannizzaro's reaction:

$$2\ R.CHO + H_2O = R.CH_2OH + R.COOH$$

"Further proof is afforded by the fact that the corresponding acid is not formed.

2. The product of reaction, when its constitution admits of it, is often optically active, showing that the reduction is carried out by an asymmetric agent and is therefore, probably a true enzyme reaction.

"Nearly all these reductions have been effected in the foregoing way, but the addition of sugar is not always essential. Thus a yield of over 50% of butylene glycol was obtained from aldol by the action of a total of 1550 g. of yeast during two months on 100 g. aldol without any addition of sugar. It must be remembered, however, that this quantitiy of yeast might contain a large proportion of glycogen (10-30%) which would gradually undergo autofermentation," p. 81.

"It may be regarded as established that the source of the hydrogen used up in the various reductions described above is either water (Bach), in which case some acceptor for the oxygen must also be present, or an oxidisable substance, which is directly capable of losing hydrogen (Wieland) and thus acts as a hydrogen donator, and great interest attaches to the nature of his compound.

"Some light is thrown on this problem by the experiments of Harden and Norris who showed that dried yeast and zymin lost the power or reducing methylene bue when they were thoroughly washed, but that this power was restored by the addition of the washings, of ordinary bouillon (peptone-beef-broth) and of various aldehydes, but not of formaldehyde or acetaldehyde. It is to be presumed that the active substances, which restored the power of reduction, were capable of acting as oxygen acceptors (or hydrogen donators) and thus enabled the "hydrolytic oxidation-reduction" to proceed. The reaction is evide ntly highly specific, as many easily oxidisable substances were inactive, including formaldehyde, which acts as the oxygen acceptor in Schardinger's reaction in milk.

"These experiments, however, do not indicate what is the actual substance which undergoes oxidation in the various phytochemical reductions enumerated above, and in order to understand this it is necessary to consider the results obtained by Neuberg and his colleagues, which are discussed later on (p. 104).

"It has been shown by them that in all probability the production of alcohol and carbon dioxide from yeast proceeds by way of pyruvic acid, which is then decomposed by the carboxylase of the yeast (p. 73) into carbon dioxide and acetaldehyde, the latter being then reduced to alcohol. The formation of pyruvic acid from glucose involves a dehydrogenation and it is the hydrogen thus removed which serves for the reduction of the aldehyde. The reactions involved may be written as follows, the final products being italicised:

1. $C_6H_{12}O_6 = 2C_3H_6O_3$.
2. $2C_3H_6O_3 = 2C_3H_4O_3 + 4H$.
3. $2C_3H_4O_3 = 2CO_2 + 2C_2H_4O$.
4. $2C_2H_4O + 4H = 2C_2H_6O$.

"It has further been shown by Neuberg (p. 103) that it is possible, in several different ways, partially to protect the acetaldehyde from reduction and that the hydrogen thus rendered available is capable of effecting another reducing action, inasmuch as equivalent quantities of glycerol ($C_3H_8O_3$) are then produced, presumably by the reduction of an intermediate substance of the formula $C_3H_6O_3$ (see equation 1). The production of pyruvic acid, according to equation 2, is thus rendered possible and the fermentation continues. This suggests the possibility that the various substances capable of reduction by yeast might be supplied with the necessary hydrogen by deviation of some of the available hydrogen from the acetaldehyde, an equivalent amount of which would thus be protected from reduction and would be found among the products of fermentation," p. 82.

Wilder D. Bancroft

Physikalisch-chemische Mineralogie und Petrologie. *Die Fortschritte in den letzten zehn Jahren. By Wilhelm Eitel. 22 × 15 cm; pp. viii + 174. Dresden and Leipzig: Theodor Steinkopff, 1925. Price: 8 marks paper, 9.20 marks bound.* In the general part the author discusses the principles of equilibrium theory; inversions; caloric properties of the minerals; two-component, three-component, four-component, and multicomponent systems; the constituents of the magmas and of the earth's crust. In the much longer special part the author considers, among other things, silicate minerals, polynary minerals, magmatic gases, zeolites, weathering, the colloid chemistry of mineralogy, dolomite, salt deposits, metamorphic rocks, and crystalline shales.

On p. 5 it is pointed out that we get nearly the same curve for chrome steel, beta brass, and foams of soap, resins or gelatine, if we plot frequency against the number of sides of the polygons. On p. 9 there is a cut of Washburn's apparatus for measuring the viscosity of molten soda-lime glasses. On p. 11 is the statement that crystallized silver iodide is more strongly dissociated electrolytically than the fused salt. The information about beta alumina, p. 36, is not up to date. This modification is formed in presence of soda and goes back to the alpha form if heated long enough to drive off the soda.

Goldschmidt concludes, p. 39, that diamonds were formed at a depth of 60-100 kilometers. According to Chaudron and Forestier, p. 84, ferrous oxide is not stable above 570°, breaking up at that temperature into metallic iron and magnetite. Sosman and Hostetter consider, p. 36, that there is a strongly ferromagnetic modification of ferric oxide. The author does not consider the possibility, p. 110, of a calcium bicarbonate solution being wholly or in part a suspension of calcium carbonate peptized by carbon dioxide.

On p. 111 is the statement that Tammann and Pape have proved that kaolin breaks into alumina and silica when the water is driven off. This may be true; but it was so stated much earlier by Mellor. There is an interesting paragraph, p. 123, on the surface tensions of crystals and on the effect of change of surface tension on the rate of growth of different fads.

Wilder D. Bancroft

Die Allgemeinheit des Kolloidzustandes. *By P. P. von Weimarn. Vol. I. Second revised and enlarged edition. 25 × 17 cm; pp. xvi + 504. Dresden and Leipzig: Theodor Steinkopff, 1925.* This is not a book on general chemistry. It is a detailed account, from an avowedly inductive viewpoint, of the author's experiments to show that any substance can be obtained in a colloidal form. The author deserves all credit for having formulated this generalization nearly twenty years ago; but nobody questions this now and nearly five hundred pages as a starter seems excessive. The author's viewpoint has not changed much and he still considers liquids and gases as crystalline, though he now prefers to call them vectorial. As a historical record the volume is valuable but that is all that can be said for it. The method of presentation and the terminology are both bad.

Wilder D. Bancroft

Lehrbuch der Mikrochemie. *By Friedrich Emich. Second edition. 25 × 16 cm; pp. 272. Munich: J. F. Bergmann, 1926. Price: 16.50 marks; 18.60 marks bound.* The demand for a second edition of Prof. Emich's standard work on micro-chemistry, and the fact that this has had to be completely rewritten affords a proof—if proof were needed—of the correctness of the Author's statement in the Preface that few branches of scientific experimental work have experienced such a rapid development as that which includes microchemical practice. There can, in fact, be no doubt that micro-chemistry is daily becoming more generally recognised and more universally accepted as an ordinary branch of chemical procedure. It has a rapidly growing, and important literature, a technique, the ingenuity and beauty of which command our admiration, and last but not least a Journal—"Mikrochemie"—which is now in the fourth year of its existence, and volumes of which appear at fairly frequent intervals.

The work under review follows in its main outline the procedure generally adopted in other works dealing with this subject, one part being devoted to what may be described as general microchemistry, and a further part dealing with certain special reactions.

The general section is divided into three sub-sections dealing with (a) qualitative analysis, (b) quantitative analysis and (c) preparations. In the special part reactions are given for groups of cations and anions much as in the case of ordinary treatises on analytical chemistry, whilst in the organic part there is a division of the subject into methane derivatives, ordinary iso-cyclic derivatives, and finally, heterocyclic compounds.

The only way in which the accuracy of a book such as this can be properly assessed is by working with it as a bench companion for some considerable time, but in glancing through the book the Reviewer has derived the impression that the information is concise and accurate. At any rate that is the case with some sections with which he is specially acquainted.

The printing is good, and the illustrations are well chosen and clearly executed. This new edition of Prof. Emich's book is one which may be very warmly and confidently commended to chemists who are compelled from time to time—whether they like it or not—to work with very small quantities of materials, and there are, in ordinary practice, as the writer of this review has found on more than one occasion, problems, the solution of which can only be accomplished by the application of micro-chemical methods. As many of the processes described deal with the determination of physical constants the book cannot fail also to appeal to physicists.

It is perhaps to be regretted that the Author still regards the completeness of Prof. Pregl's handbook on elementary quantitative organic analysis a sufficient reason for dismissing that important subject in a page-and-a-half. There is, moreover, a tendency here and there to recommend a more or less complicated micro-chemical method where a simpler one is available, but these are slight defects in a work which, speaking generally, may be regarded as an admirable exposition of the subject.

A. Chaston Chapman

SOLUTIONS FOR COLORIMETRIC STANDARDS. I. SPECTRAL TRANSMISSION CURVES FOR SOME AQUEOUS SOLUTIONS CONTAINING ORGANIC INDICATORS OR INORGANIC SALTS

BY M. G. MELLON AND F. D. MARTIN

In undertaking a general study of the standards employed in various colorimetric analytical procedures, attention has been directed first to the set of indicators proposed by Clark and Lubs[1] for the determination of the concentration of hydrogen ions, and to the inorganic solutions suggested by Arny and his students[2] for general colorimetric work. The object of the present paper is to report the results of certain spectrophotometric measurements made on systems containing these materials.

Color and Its Determination

The precise specification of characteristics which serve to distinguish an object exhibiting color is a matter involving considerable confusion and lack of uniformity in present practice. To state, for example, that the object is blue means little, for one might have in mind, in hue alone, anything ranging from that of Prussian blue to that of crystallized cupric sulfate. This unsatisfactory state of affairs existing in connection with the use and significance of colors is well recognized by the physicists. A general survey of the problem has recently been made by their colorimetry committee, the results of which have been published in a distinctly worthwhile report.[3]

As an introduction to the work being undertaken in this laboratory on solutions as standards of color, mention may properly be made of certain definitions and conclusions formulated by the committee on colorimetry, to which reference has just been made, and by a similar committee on spectrophotometry[4]. The quotations below have been taken from the reports of these two committees.

The entity color may be defined as "*the general name for all sensations* arising from the activity of the retina of the eye and its attached nervous mechanism, this activity being, in nearly every case in the normal individual, a specific response to radiant energy of certain wave-lengths and intensities." For solutions it is the result of the modification of the incident light by selective absorption of certain frequencies in the visible region of the spectrum. Any color can be completely specified psychologically by three fundamental characteristics, for which the following nomenclature has been suggested:

"Brilliance is that attribute of any color in respect of which it may be classed as equivalent to some member of a series of grays ranging from black

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[1] J. Bact. **2**, 1, 109, 191 (1917).

[2] Rept. 8th. Int. Congr. Appl. Chem. **26**, 319 (1912); J. Am. Pharm. Assoc. **2**, 76 (1913); Drug. Circ. **58**, 131 (1914); J. Franklin Inst. **180**, 199 (1915).

[3] Troland et al: J. Optical Soc. America,—Rev. Sci. Instruments, **6**, 527 (1922).

[4] Gibson et al: J. Optical Soc. America,—Rev. Sci. Instruments, **10**, 169 (1925).

to white." It is expressed as percent relative brightness, and indicates the portion of the total amount of white light (light with a spectral distribution of sunlight) falling upon a body which is reflected or transmitted. Absolute black has a brightness of zero and pure white 100 percent; that for any other color falls between.

"Hue is that attribute of certain colors in respect of which they differ characteristically from the gray of the same brilliance and which permits them to be classed as reddish, yellowish, greenish, or bluish. Dominant wave-length serves to express hue.

"Saturation is that attribute of all colors possessing hue which determines their degree of difference from a gray of the same brilliance." That is, it determines the degree in which the color possesses hue. It is expressed as percent purity, and denotes how red (or yellow, etc.) the color is.

As an example of the usage of these terms one might describe a color as having a brightness of 50 percent, a dominant wave-length of 690mμ, and a purity of 85 percent. In this case the brightness is moderately great, the dominant wave-length lies in the red portion of the visible spectrum, and the degree of saturation is relatively large. One would picture a fairly bright red. A red and pink having the same dominant wave-length will differ in the percent purity, the pink being the lower of the two, since it is an unsaturated red; that is, one having white admixed with it. The greater portion of white will give the pink a higher percent brightness than the red.

"The color of an object, considered as an impression which the object produces on the observer, is determined by at least three sets of factors: (1) the physical characteristics of the object, (2) the physical characteristics of the radiant energy falling upon or emitted by it, (3) and the nature and condition of the observer's visual apparatus. Our control over color in its technical applications is confined almost exclusively to the first two sets of factors, although the ultimate goal is always to be found in the consciousness of some observer. Practical colorimetry is therefore concerned with means for the unambiguous designation of those properties of objects and radiation which determine color perception."

The satisfactory determination of the colorimetric characteristics for a given system involves the determination of definite physical properties of the system, and the statement of the results obtained in terms which are likewise definite. "Most of the means actually employed, however, utilize the visual apparatus of an observer as an essential element, and hence are frequently not independent of the nature and special condition of this apparatus."

For the specification and testing of color in technical work there have come into more or less extensive use several systems which are arrangements based upon color matching with arbitrary standards, such as colored glasses for tintometers or variegated pigments for the systems of Munsell, Ridgway, or Ostwald. To specify a color by reference to stimuli by these methods involves the specification of a stimulus empirically found to evoke the same color.

But when one desi on the side of the stimulus, the fundamental method of colorimetric specification a spectrophotometric method is employed. By

means of the spectrophotometer one can specify the identical radiant energy actually evoking the color, and at the same time take advantage of a procedure which is actually independent of the observer. "The characteristics of physical objects which determine their colors, when viewed by radiation from other sources, can be expressed almost completely by means of spectral reflection or transmission curves, representing as a function of the wave-length or frequency, the fraction of the original radiation impinging upon the object, which finally leaves it as reflected or transmitted rays, respectively. Such curves are most readily determined by means of a spectrophotometer. For the intercomparison of the color values of objects, without reference to the radiation by which they are viewed or the observer's visual system, reflection or transmission curves are of great value in colorimetrics, although such curves represent properties of objects rather than of immediate stimuli to color."

A spectrophotometer was selected, therefore, as the proper instrument to use in determining the desired measurement of the colorimetric characteristics of the solutions under consideration.

Spectrophotometric Data

Spectrophotometric measurements on solutions, as carried out in this work, involve the determination of the transmittancies of the solutions; that is, the ratio of the transmission of a given cell containing the solution to the transmission of a duplicate cell containing pure solvent. Two colors may then be compared by simply comparing their transmittancy curves, the curve for any color conveying to the mind of an experienced observer something of the characteristics of the color itself.

In the direct use of such curves certain facts should be kept in mind[1]. "Two colors which appear to match under one illumination may not appear to match under another. It is possible for two colors which appear matched in daylight to have the same brightness, dominant wave-length and purity, and yet each yield an entirely different spectral distribution curve when measured on a spectrophotometer. If, however, the two colors yield the same curve, they will not only have the same brightness, dominant wave-length and purity, but will appear matched under any illumination whatever." Priest[2] has shown that "if any two lights, however, different in spectral distribution, excite colors of the same quality, the wave-lengths of the center of gravity of their spectral distributions are coincident." But "two spectral distributions of light may have the same wave-lengths of center of gravity and not excite colors of the same quality if the lights in the two cases are distributed over different ranges of wave-length."

Although spectrophotometric data constitute a fundamental specification of a color stimulus, as such, and may be of wide use without conversion to other terms, it should be noted that one may desire to specify the color

[1] Keuffel and Esser: Technical Bulletin with Color Analyzer.

[2] J. Optical Soc. America—Rev. Sci. Instruments, 4, 388 (1920).

stimulus in terms of the sensation it produces rather than to use the curve itself. Such curves suffer as a means of colorimetric specification in that they cannot readily be interpreted as color.

In some cases it is advantageous to use the trichromatic system which involves a calculation of the elementary color excitation values; that is, the percentage red, green and violet excitations produced by the color of the given sample. To become determinative of a definite color in this manner spectral distribution curves "require combination with a certain energy distribution, representative of the particular source by which the object is viewed." A given solution might then be designated as producing a sensation of 5 percent violet, 20 percent green, and 75 percent red.

In other cases the specification of the three attributes of color—brilliance, hue, and saturation—for any given color completely describes the color as it appears in sunlight to the normal eye. As already indicated, a color may then be described as having, for example, a brightness of 40 percent, a dominant wave-length of 500mμ, and a purity of 70 percent. The determination of these characteristics is known as monochromatic analysis.

Apparatus and Materials

The spectrophotometer used was a Keuffel and Esser color analyzer with a constant deviation spectrometer and disk photometer which gave direct readings for wave-length and percentage transmission. This instrument has been sufficiently described by Brode[1], by Keuffel[2], and by Ferry[3].

In using the analyzer settings of the sector for 0, 25, and 100 percent were checked at the beginning of each day's run, while the wave-length scale was checked with the yellow D line of the sodium flame for every second sample. Although a precision of one percent is claimed for the instrument, it is doubtful whether this limit was reached. The eye rather quickly lost its sensitivity to small differences in intensity during a long series of readings, especially in the violet region, where the sensitivity is not very great under normal conditions. Frequent shifts from one eye to the other help to reduce this fatigue. Also some lost motion was encountered in adjusting the photometer disks. The errors resulting were partly compensated by taking the average of several readings. Part of the data were obtained by setting the instrument for a given transmittancy and reading the wave-length for that transmittancy, and part by the reverse process.

The solutions were contained in glass-lined cells 5 cm in length. One contained the solvent alone, and the other the solvent plus the compound being measured. 100 watt, nitrogen-filled, tungsten bulbs (with 110 volt, A. C. current) were used in the analyzer. While the temperature of the room varied from 22° to 26°C. during the entire work, the change during the determination on any one solution was not over one degree.

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[1] J. Am. Chem. Soc., **46**, 581 (1924).
[2] J. Optical Soc. America—Rev. Sci. Instruments, **11**, 403 (1925).
[3] "Physics Measurements," I, 239 (1926).

Commercial indicators were used, the solutions indicated in Table I being prepared as follows: thymol blue, brom-phenol blue, brom-cresol purple, brom-thymol blue, phenol red, and cresol red by the method of Clark[1], using aqueous solutions of the alkali salts; the newer indicators of Cohen[2]—chlor-phenol red, brom-phenol red, brom-chlor-phenol blue, and brom-cresol green—by the same procedure; methyl red was dissolved in 50 percent ethyl alcohol, while the 95 percent solution was used for ortho-cresolphthalein, phenol-phthalein, and the nitro-phenols (the latter were adjusted with sodium hydroxide or hydrochloric acid until practically colorless); and methyl orange was prepared in aqueous solution.

TABLE I
Indicators used

Name	Concentration	pH Range	pH of Buffers
1.—Methyl orange	0.05%	3.0– 4.6	2.4– 5.0
2.—Thymol blue	0.04	1.2– 2.8	1.0– 3.2
3.—Brom-phenol blue	0.04	3.0– 4.6	2.4– 5.0
4.—Methyl red	0.05	4.4– 6.0	4.0– 6.4
5.—Brom-cresol purple	0.04	5.2– 6.8	4.8– 7.2
6.—Brom-thymol blue	0.04	6.0– 7.6	5.6– 8.0
7.—Phenol red	0.02	6.8– 8.4	6.4– 8.8
8.—Cresol red	0.02	7.2– 8.8	6.8– 9.2
9.—Thymol blue	0.04	8.0– 9.6	7.6–10.0
10.—2, 4 dinitrophenol	0.04	2.0– 4.7	— – 4.8
11.—p-nitrophenol	0.04	5.0– 7.0	— – 7.4
12.—m-nitrophenol	0.04	6.3– 9.0	— – 9.4
13.—Phenolphthalein	0.04	8.3–10.0	— –10.2
14.—Cresolphthalein	0.04	8.2– 9.8	— –10.2
15.—Chlor-phenol red	0.04	5.0– 6.6	4.6– 7.0
16.—Brom-phenol red	0.04	5.4– 7.0	5.0– 7.4
17.—Brom-chlor-phenol blue	0.04	3.2– 4.8	2.8– 5.2
18.—Brom-cresol green	0.04	4.0– 5.6	3.6– 6.0

The buffer solutions for the indicators were selected with pH values sufficiently above or below the normal range of the indicator to insure practically complete transformation to either the basic or acidic form. These solutions were prepared according to the directions of Clark[3], using salts which had been recrystallized three times from conductivity water.

In preparing the inorganic solutions cupric sulfate, cobaltous chloride, ammonium dichromate, and potassium dichromate were recrystallized from conductivity water. Ferric chloride was obtained by passing chlorine over ferric oxide heated in a combustion furnace and the product sublimed. Chloro-pentammino-cobaltic chloride was prepared by the method of Willard[4]. In

[1] "Determination of Hydrogen Ions," p. 80 (1923).
[2] U. S. Public Health Reports, **38**, 199 (1923).
[3] "Determination of Hydrogen Ions," p. 106 (1923).
[4] J. Am. Chem. Soc., **44**, 2220 (1920).

standardizing the solutions the copper and cobalt were determined electrolytically, and iron and chromium gravimetrically. The potassium dichromate was weighed directly. Solutions of cupric sulfate, ferric chloride, and cobaltous chloride were made to contain one percent hydrochloric acid, as recommended by Arny[1]. The ammoniacal solutions of cupric sulfate, ammonium chromate, and chloro-pentammino-cobaltic chloride contained 2.8 percent ammonia. In diluting any of these solutions, the concentration of acid or base was kept constant. An aqueous solution of potassium dichromate was used. All these solutions were preserved in Pyrex glass in the dark and showed no visible evidence of decomposition after standing a year, except for traces of a precipitate in the solution of ammoniacal cupric sulfate.

In his directions for the preparation of the standards for the determination of the concentration of hydrogen ions Clark[2] recommends the addition of specified amounts of the solution of the indicator, prepared on a percentage basis, to a definite amount of the buffer solution—usually 5 drops of the indicator, of the concentration shown in Table I, to 10 ml of the buffer. Since one of the objects in mind was to determine the colorimetric characteristics of these standards, it seemed advisable in this case to follow the recommended procedure for preparing solutions rather than to use the molar system for expressing concentrations. Assuming that 1 ml is equivalent to 25 drops, the solution prepared by adding 1 ml of the solution of the indicator to 50 ml of the buffer solution represented a concentration approximately equal to that mentioned above. One or more solutions of other concentrations were measured for each compound.

Experimental Data

Figs. 1-10 show the data obtained. The curves are plotted with wavelengths as abscissa on an ordinary scale and percent transmittancy as ordinates on a logarithmic scale. Appel and Brode[3] noted that this type of curve gives a good representation of the absorption as it appears to the eye. These investigators used the negative logarithm of the transmittancy as the ordinates. This quantity is, on the basis of Beer's Law, directly proportional to the product of the concentration and thickness.

Discussion and Summary

A discussion of the general significance of the data presented, in relation to the use of solutions for colorimetric standards, is reserved for a later communication.

As already indicated, spectral transmission curves serve as fundamental data for various uses. With the curve determined, one may calculate values for the color sensation that will be experienced for illumination by a given source, providing the spectral distribution of the source is known. General

[1] J. Franklin Inst., **180**, 199 (1915).
[2] "Determination of Hydrogen Ions," p. 49 (1923).
[3] Ind. Eng. Chem., **16**, 797 (1924).

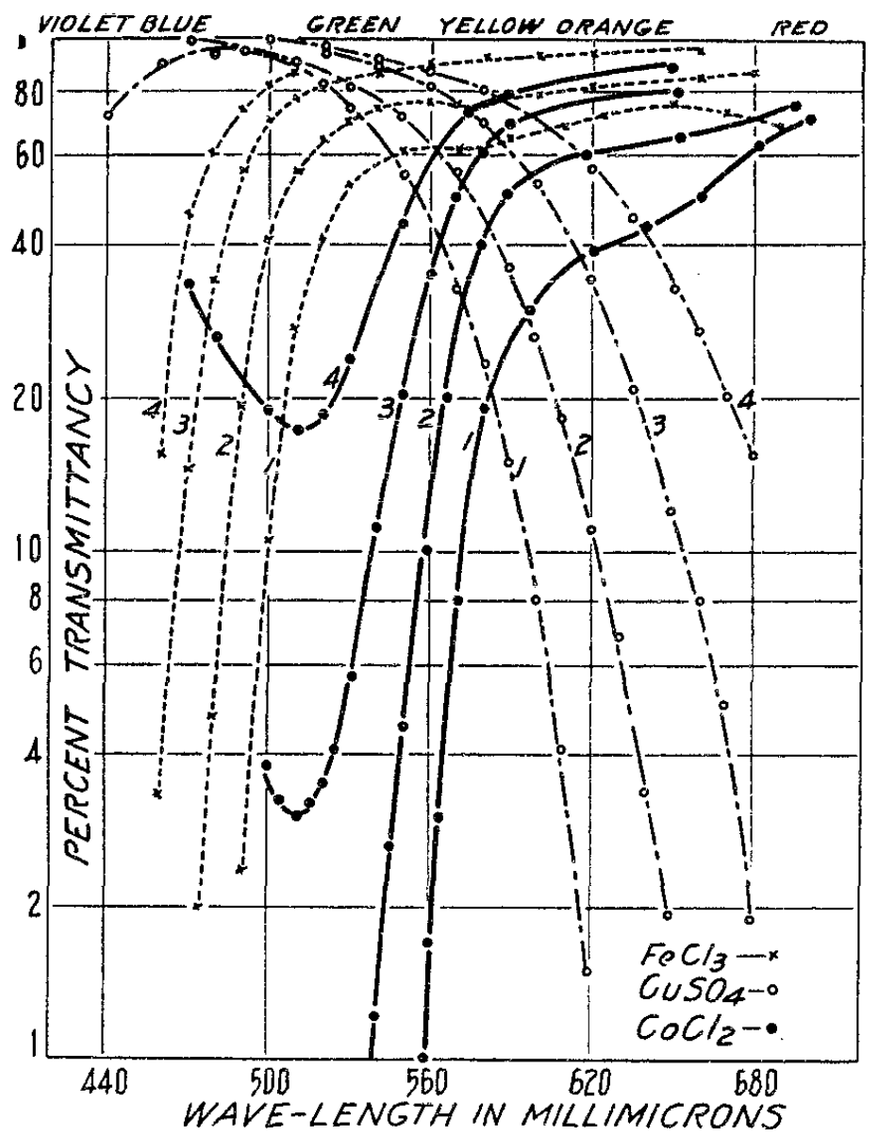


FIG. 1

Spectral transmission curves for the following systems: aqueous solution (containing 1% hydrochloric acid) of cupric sulfate, ferric chloride, and cobaltous chloride. For each of these salts curves 1, 2, 3 and 4 are for M/4, M/8, M/16, and M/32 solutions, respectively.

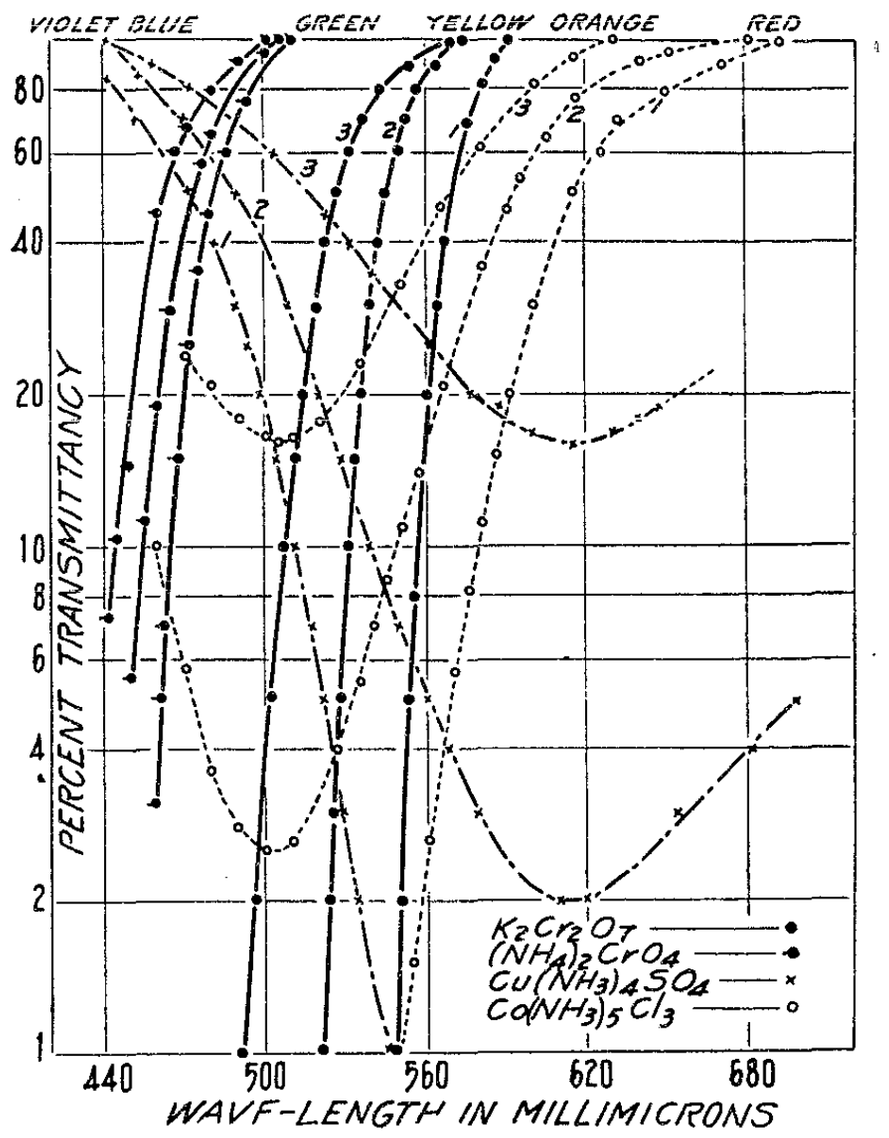


FIG. 2

Spectral transmission curves for the following systems: aqueous solution of potassium dichromate—curves 1, 2 and 3 are for M/6, M/60 and M/300 solutions, respectively; aqueous solution (containing 2.8 percent of ammonia) of ammonium chromate—curves 1, 2 and 3 are for M/300, M/600 and M/1200 solutions, respectively; and aqueous solutions (containing 2.8 percent ammonia) of tetrammino-cupric sulfate and chloropentammino-cobaltic chloride—for each of these salts curves 1, 2 and 3 are for M/100, M/200 and M/400 solutions, respectively.

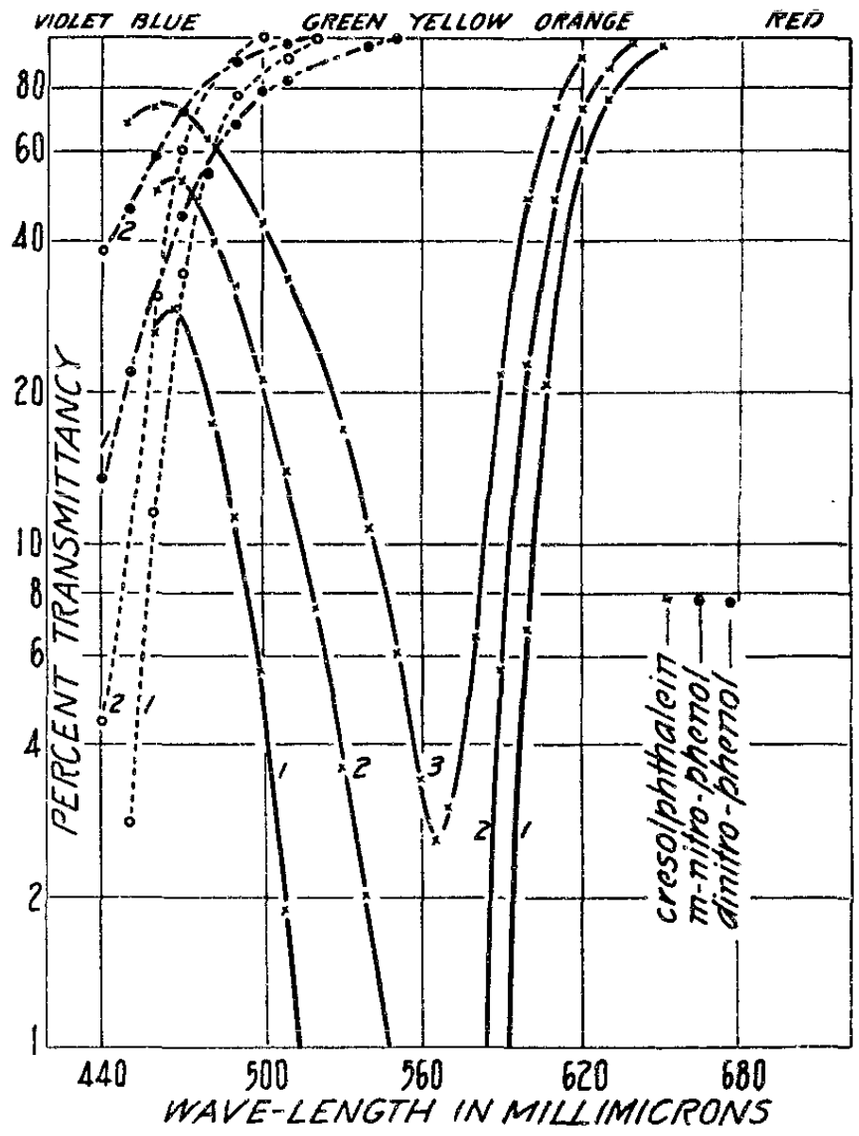


FIG. 3

Spectral transmission curves for the following systems: cresolphthalein at pH 10.2—curves 1, 2 and 3 are for 1.0, 0.5 and 0.25 ml, respectively, of the indicator solution in 50 ml of buffer solution; and m-nitro-phenol at pH 9.4 and dinitro-phenol at pH 4.8—curves 1 and 2, for each of these indicators, are for 4 and 2 ml, respectively, of the indicator solution in 50 ml of buffer solution.

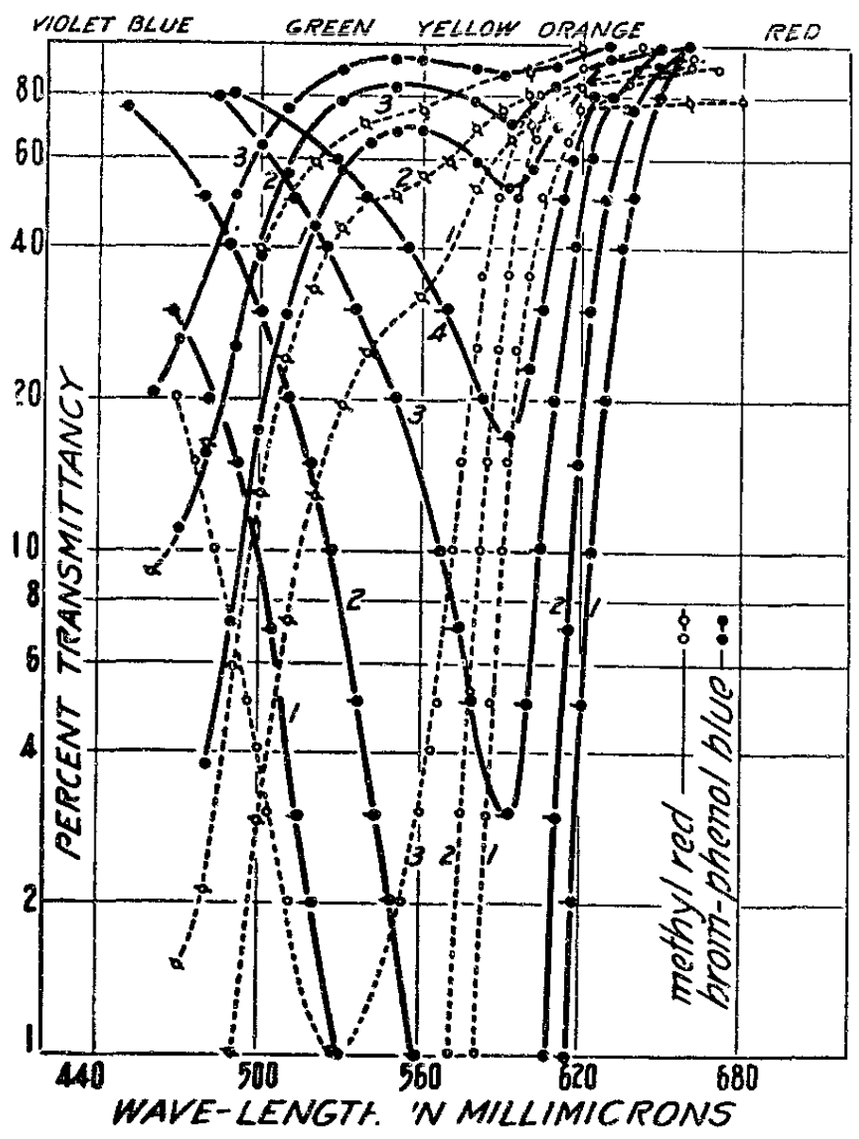


FIG. 4

Spectral transmission curves for the following systems: methyl red at pH 6.4 (circles with line)—curves 1, 2 and 3 are for 4.0, 2.0 and 1.0 ml, respectively, of the solution of the indicator in 50 ml of the buffer solution; methyl red at pH 4.0 (circles)—curves 1, 2 and 3 are for 5.0 and 2.5 and 1.25 ml, respectively, of the solution of the indicator in 50 ml of the buffer solution; brom-phenol blue at pH 5.0 (dots with line) and at pH 2.4 (dots)—curves 1, 2 and 3 in each case are for 2.0, 1.0 and 0.5 ml, respectively, of the solution of the indicator in 50 ml of the buffer solution, while curve 4 is for 0.25 ml of the solution of the indicator.

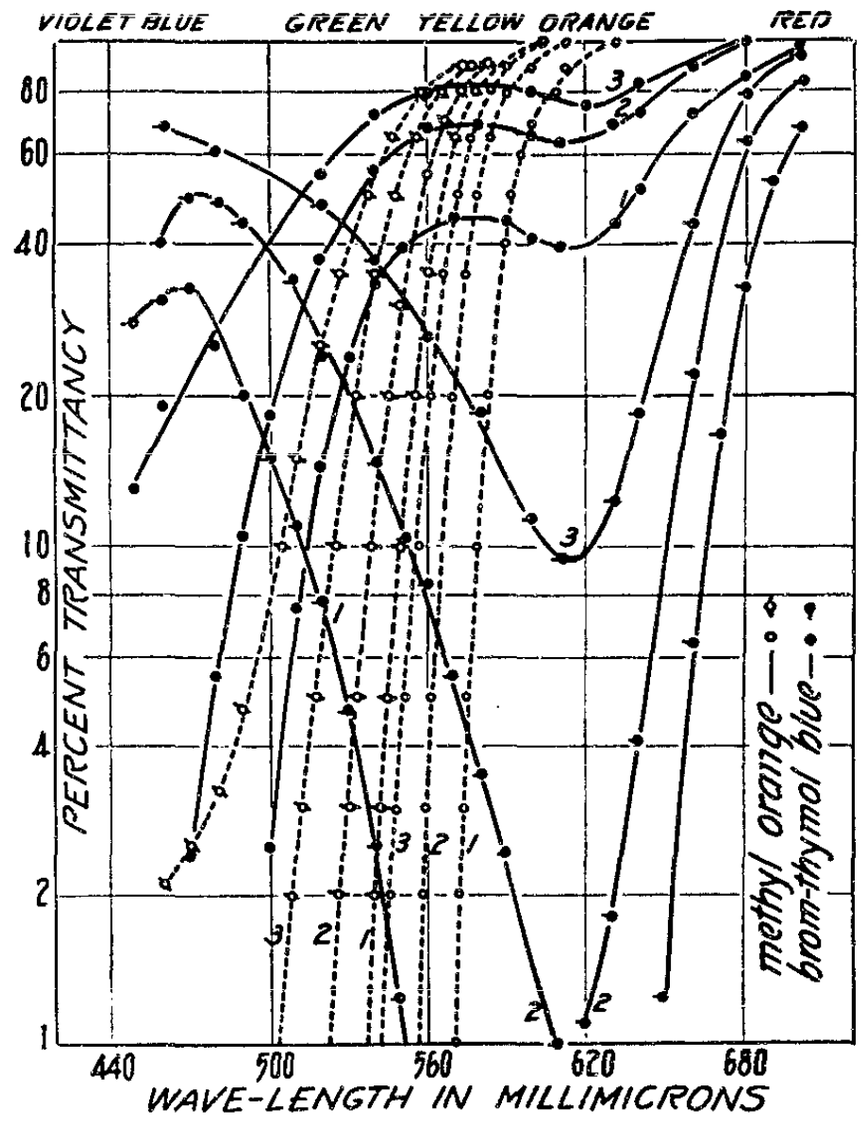


FIG. 5

Spectral transmission curves for the following systems: methyl orange at pH 5.0 (circles with line —curves 1, 2, 3 and 4 are for 5.0, 2.5, 1.25 and 0.625 ml, respectively, of the solution of the indicator in 50 ml of the buffer solution; methyl orange at pH 2.4 (circles)—curves 1, 2 and 3 are for 5.0, 2.5 and 1.25 ml, respectively, of the solution of the indicator in 50 ml of the buffer solution; brom-thymol blue at pH 8.0 (dots with lines)—curves 1, 2 and 3 are for 2.0, 1.0 and 0.5 ml, respectively, of the solution of the indicator in 50 ml of the buffer solution; and brom-thymol blue at pH 5.6 (triangles)—curves 1, 2 and 3 are for 4.0, 2.0 and 1.0 ml, respectively, of the solution of the indicator in 50 ml of the buffer solution.

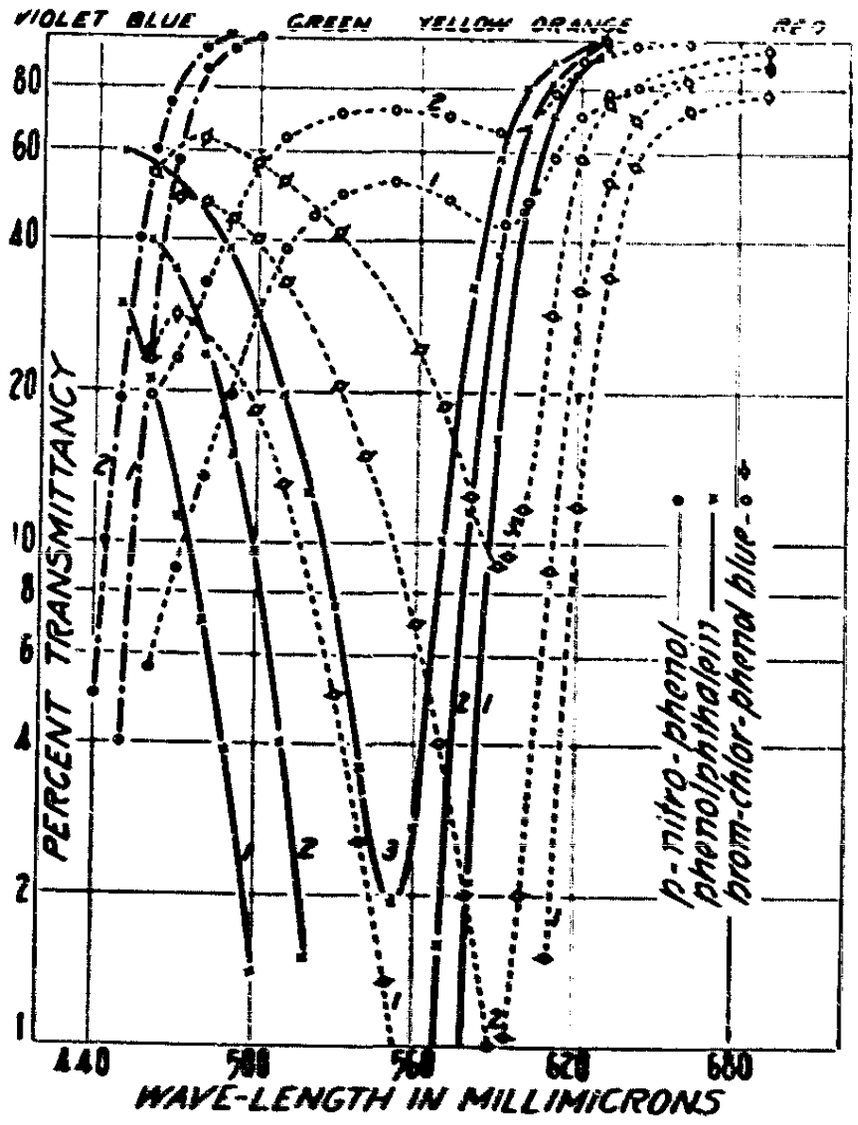


FIG. 6

Spectral transmission curves for the following systems: p-nitrophenol at pH 7.4—curves 1 and 2 are for 2 and 1 ml. respectively, of the indicator solution in 50 ml of buffer solution; phenolphthalein at pH 10.2—curves 1, 2 and 3 are for 2.0, 1.0 and 0.5 ml. respectively, of the indicator solution in 50 ml of buffer solution; and brom-chlor-phenol blue at pH 2.8 (circles) and at pH 5.2 (circles with line)—curves 1 and 2 for each pH value are for 2 and 1 ml. respectively, of the indicator solution in 50 ml of the buffer solution, while curve 3 is for 0.5 ml in the same volume of buffer solution.

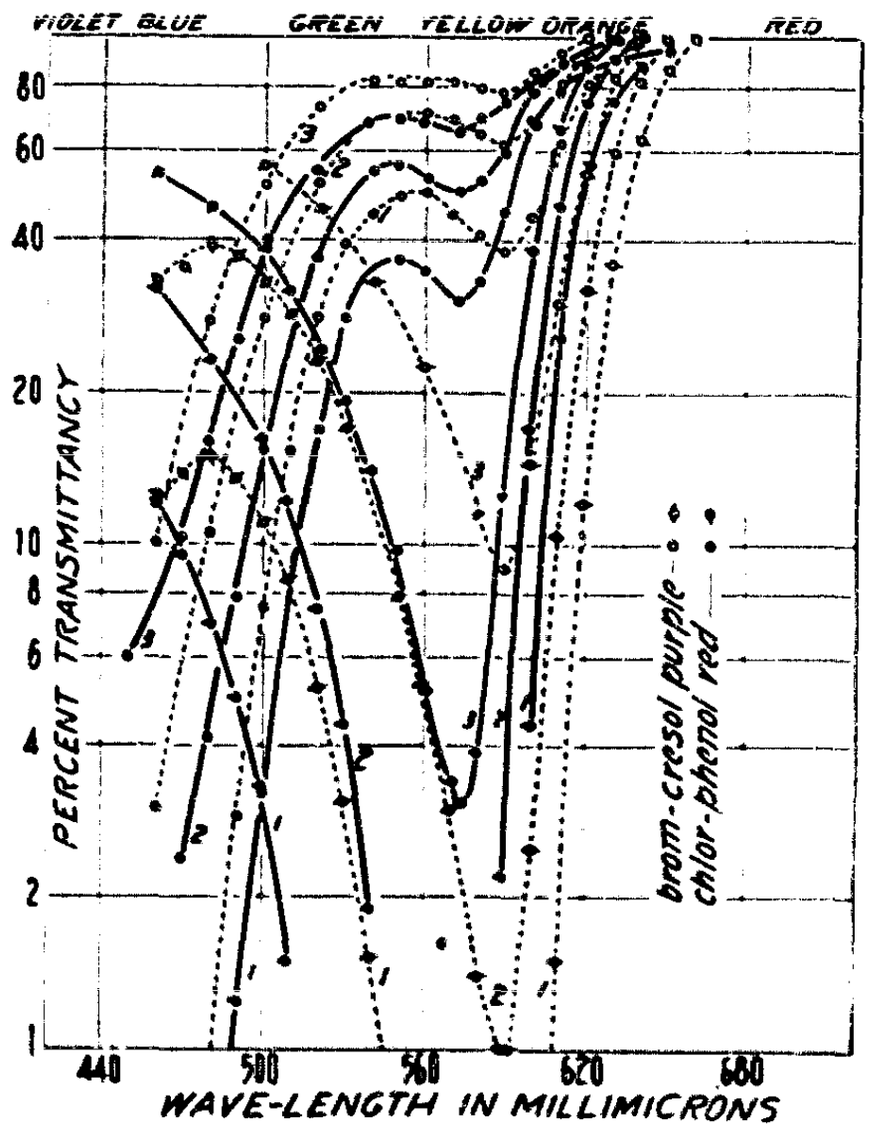


FIG. 7

Spectral transmission curves for the following systems: brom-cresol purple at pH 4.8 (circles) and chlorphenol red at pH 4.6 (dots)—curves 1, 2 and 3 are for 4.0, 2.0 and 1.0 ml. respectively, of the solution of the indicator in 50 ml of the buffer solution; and brom-cresol purple at pH 7.2 (circles with line) and chlor-phenol red at pH 7.0 (dots with line)—curves 1, 2 and 3 are for 2.0, 1.0 and 0.5 ml. respectively, of the solution of the indicator in 50 ml of the buffer solution.

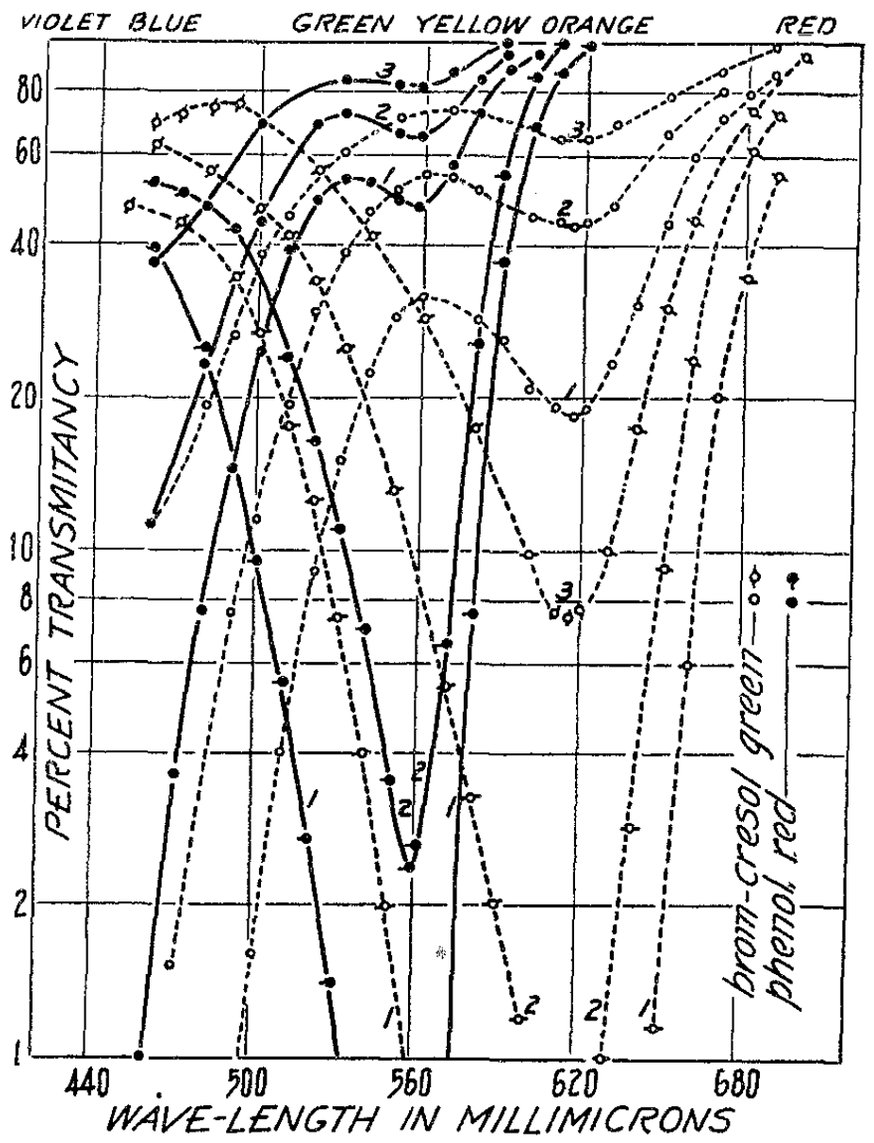


FIG. 8

Spectral transmission curves for the following systems: brom-cresol green—at pH 6.0 (circles with line)—curves 1, 2 and 3 are for 2.0, 1.0 and 0.5 ml, respectively, of the solution of the indicator in 50 ml of the buffer solution; brom-cresol green at pH 3.6 (circles)—curves 1, 2 and 3 are for 4.0, 2.0 and 1.0 ml, respectively, of the solution of the indicator in 50 ml of the buffer solution; phenol red at pH 8.8 (dots with line —curves 1 and 2 are for 1.0 and 0.5 ml, respectively, of the solution of the indicator in 50 ml of the buffer solution; and phenol red at pH 6.4 (dots)—curves 1, 2 and 3 are for 2.0, 1.0 and 0.5 ml, respectively, of the solution of the indicator in 50 ml of the buffer solution.

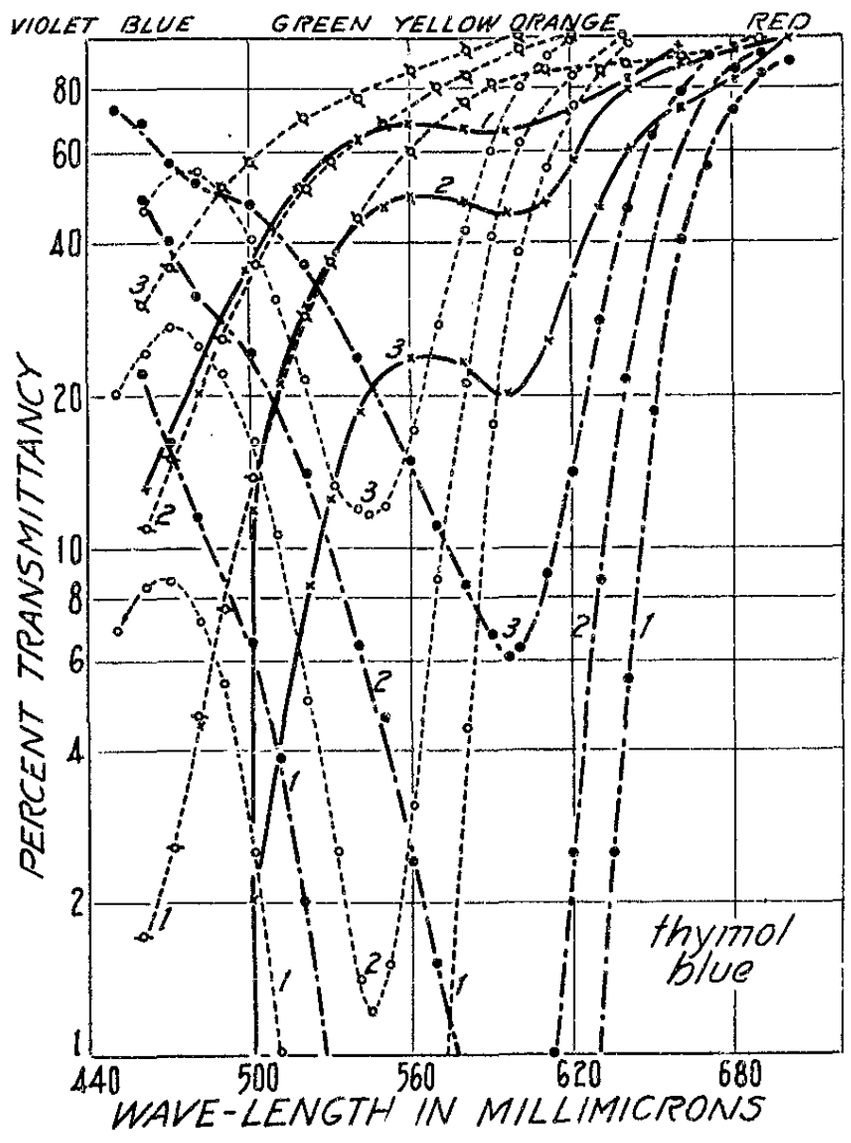


FIG. 9

Spectral transmission curves for thymol blue for the following pH values: 1.0 (circles), 3.2 (circles with line), 7.6 (crosses), and 10.0 (dots). For pH values 1.0, 3.2 and 10.0 curves 1, 2 and 3 are for 2.0, 1.0 and 0.5 ml, respectively, of the solution of the indicator in 50 ml of the buffer solution. For pH value 7.6 curves 1, 2 and 3 are for 4.0, 2.0 and 1.0 ml, respectively, of the solution of the indicator in 50 ml of the buffer solution.

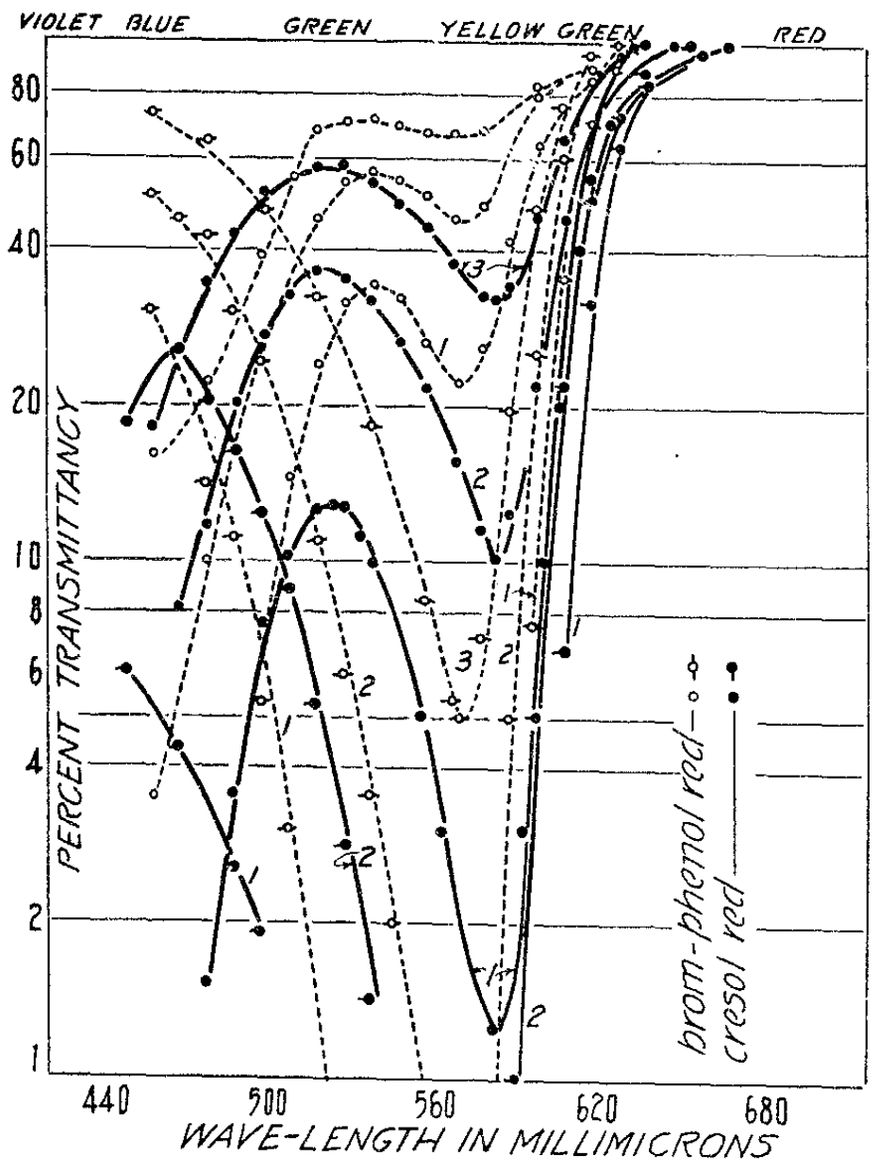


FIG. 10

Spectral transmission curves for the following systems: brom-phenol red at pH 7.4 (dots with line)—curves 1 and 2 are for 2.0 and 1.0 ml, respectively, of the solution of the indicator in 50 ml of the buffer solution; brom-phenol red at pH 5.0 (dots) and cresol red at pH 9.2 (circles with line —curves 1, 2 and 3 in each case are for 2.0, 1.0 and 0.5 ml, respectively, of the solution of the indicator in 50 ml of the buffer solution; and cresol red at pH 6.8 (circles)—curves 1, 2 and 3 are for 4.0, 2.0 and 1.0 ml, respectively, of the solution of the indicator in 50 ml of the buffer solution.

information relating to this calculation and to the specification of color in terms of relative brightness, dominant wave-length and purity are included in the references mentioned.[1]

It should be noted that Brode[2], in proposing a spectrophotometric method for the determination of the concentration of hydrogen ions in solutions of dyes, presented curves for several indicators, using a single concentration of the indicator in solutions of different pH values. The present measurements on the transmittancy in the visible range for a number of systems furnishes a check on the minimum point of his curves; that is, the wave-length of maximum absorption. Also it includes, in addition to data for Arny's solutions of inorganic salts, data for the same indicators at other concentrations, and for a number of other indicators, including four of those recently proposed by Cohen.

Purdue University,
Lafayette,
Indiana.

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[1] Troland et al: J. Optical Soc. America.—Rev. Sci. Instruments, **6**, 527 (1922); Gibson et al.: **10**, 169 (1925); Ferry: "Physics Measurements", **1**, 239 (1926).

[2] J. Am. Chem. Soc., **46**, 581 (1924).

-58

THE CATALYTIC MINIMUM POINT. II. THE IODINE-ACETONE REACTION IN BUFFER SOLUTION*

BY MILTON BERGSTEIN**

The iodine-acetone reaction has been investigated to some extent in the past because of its apparent simplicity. Dawson and Powis[1] after extensive studies of the reaction in acid solution came to the conclusion that the velocity of the reaction is directly proportional to the concentrations of acetone and acid and independent of the concentration of iodine. Rice and his co-workers[2] also studied the ketone-halogen reactions catalyzed by acids and in passing arrived at the same conclusion.

The former investigators found in studying the autocatalyzed reaction

$$CH_3COCH_3 + I_2 \longrightarrow CH_3COCH_2I + H^+ + I^-$$

in distilled water that the initial velocity (determined by extrapolation to zero time) is considerably greater than that readily accounted for on the assumption that hydrogen ion alone is active in pure water (water of approximately pH 7) and concluded after several experiments that the initial speed in neutral solution is due to some substance or substances, the activity of which is greatly depressed by the addition of an acid and suggested one of basic nature. This autocatalyzed reaction has been studied further as previously reported.[3] The phenomena observed were used to determine the point of minimum velocity (the catalytic minimum point) of this reaction and to test the effect of variation of temperature and of concentration of neutral salt on the minimum point.

Rice and his coworkers found in the course of their work, in attempting to stop the reaction by running the mixture into approximately neutral buffer, that the reaction was not stopped, that it continued at considerable speed, and that at this pH of approximately 7 it went to completion within a day. Accordingly it was considered advisable to make some study of a ketone-halogen reaction in alkaline solution and particularly near the neutral point of pure water. This paper is the report of such an investigation. There is further reported a direct determination of the catalytic minimum point in buffer solution. The iodine-acetone reaction was selected for particular study.

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* Contribution from the Research Laboratory of the Photion Instrument Corporation.

** Taken in part from a thesis submitted to the faculty of the Graduate School of New York University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June 1925.

[1] Dawson: J. Chem. Soc., **99**, 1 (1911); Dawson and Powis: **101**, 1503 (1912); **105**, 1093 (1914).

[2] Rice and Kilpatrick: J. Am. Chem. Soc., **45**, 1361 (1923); Rice and Lemkin: **45**, 1896 (1923); Rice: **45**, 2808 (1923); Rice, Fryling, and Wesolowski: **46**, 2405 (1924); Rice and Fryling: **47**, 379 (1925).

[3] Bergstein and Kilpatrick: J. Phys. Chem., **30**, 1616 (1926).

Catalysis near the Neutral Point of Pure Water

All the experiments reported in this part were conducted at 25° ±.02 in the standard sodium-potassium phosphate buffer mixtures of Sörensen recommended by Clark.[1] A series of determinations (not recorded herein) at arbitrary phosphate concentrations showed that the rate of the reaction

$$CH_3COCH_3 + I_2 + OH^- \longrightarrow CH_3COCH_2I + H^+ + I^- + OH^-$$

is directly proportional to the concentration of acetone and apparently does not depend on the concentration of iodine. The H^+ ion liberated is without effect on the rate of the reaction since it is immediately neutralized by the buffer. This point is discussed later.

In some experiments (also not recorded here) it was attempted to study the rate of this reaction in a buffer from the initial point to the end of the reaction. This was found impracticable. Solutions were made up in volumetric flasks by adding the required weights of buffer salts to solutions of potassium iodide and iodine in the quantities desired, and filling not quite to the mark with distilled water. In the procedure finally adopted a known weight of acetone was added from a calibrated pipette, the flask was filled to the mark with distilled water and thoroughly shaken, and, by means of a quick-running syphon, the solution was then transferred to glass-stoppered reaction vessels which held about 80 cc each. The reaction vessels were immediately placed in the thermostat. Zero time was noted (for the sake of reference and not because it was needed in the calculations) as the time when the acetone started to run into the solution. The time elapsed from zero time to that when the flasks were placed in the thermostat was usually less than four minutes and never over five. A method can be devised whereby the initial iodine concentration may be known in order to study the reaction in its entire range. However, acetone has a positive heat of solution in water, and the dissolving of 10 to 20 cc in a liter of solution has a temperature effect which influences the velocity of the reaction appreciably. It was for this reason, also, that the solutions were brought only approximately to the temperature of the thermostat before starting the reactions. The first samples were removed from the reaction vessels with calibrated pipettes at least fifteen minutes after they were introduced into the thermostat. It was found by making heating and cooling curves that the contents of flasks such as used always reached the temperature of the thermostat within that time. The samples were run into known quantities of standard sodium thiosulfate solution and titrated using starch to the disappearance of blue with thiosulfate solution from a weight burette. It was found, as reported by Rice and Fryling, that the employment of a blue light-source facilitated observation of the end-point. The time noted as final in each case was that when the sample started to run into the thiosulfate solution.

To determine the velocity constants for an experiment the titre in grams of sodium thiosulfate solution was plotted against the time and drop in titre per minute calculated directly from the graph. It should be noted that the concentration of acetone in all these runs was practically constant since it was

[1] Clark: "The Determination of Hydrogen Ions," 2nd Ed., p. 114 (1923).

so much in excess of the concentration of iodine. Fig. 1 (Experiment 164 c) is an example of the type of curve obtained. It may be noticed that there are two very flat portions. In the experiments excluding 164b and 164c these flat portions appeared to be two intersecting straight lines. The velocity constants k_1 and k_2 are for the first and second "straight" lines respectively. They are calculated from the formula

$$k = \frac{\text{drop/min.} \times \text{molarity } Na_2S_2O_3}{\text{cc of sample} \times \text{molar conc. of } (CH_3)_2CO}.$$

Table I gives the results of a typical experiment. Time is expressed in minutes. Titre is expressed in grams of sodium thiosulfate solution per volume of sample taken.

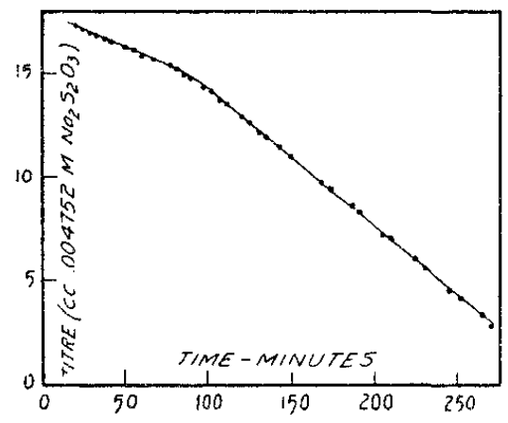


FIG. 1

Exp. 164 c. Iodine-acetone reaction in Phosphate buffer of P_H 6.813, $[H^+] = 1.56 \times 10^{-7}$; 0.2% KI; 24.91 cc samples.

TABLE I

Exp. 154 a Iodine-acetone reaction at pH 6.813, $[H^+]$ 1.56×10^{-7}.
1 L of solution containing 15.876 g acetone; 3.22% KI.

.005145 M $Na_2S_2O_3$		24.92 cc samples	
Time	Titre	Time	Titre
19	24.28	112	17.15
24	24.04	118	16.67
29.5	23.72	145	13.73
34	23.39	150	13.38
43	22.87	180	9.92
48	22.55	186	9.44
77	20.53	239	3.53
82	20.12	245	2.89
$k_1 = .451 \times 10^{-4}$		$k_2 = .822 \times 10^{-4}$	

In the group of experiments summarized in Table II an attempt was made to study the effect of a variation in concentration of potassium iodide upon the rate of reaction.

TABLE II

Effect of Concentration of Potassium Iodide on Velocity Constants at pH 6.813, $[H^+]$ 1.56×10^{-7}

Exp.	% KI	KI, N	$k_2 \times 10^4$	$k_1 \times 10^4$	I_1
164c	0.2	0.014	0.927	0.445	0.00093
124	.4	.027	——	.537	——
154d	.407	.028	.924	.473	.00146
154c	.830	.057	.909	.535	.00150
154b	1.6	.120	.852	.473	.00206
154f	2.4	.164	.831	.477	.00309
154e	3.21	.220	.824	.455	n
154a	3.22	.221	.822	.451	n
164b	5.01	.343	.809	.405	n

In the graphs of the individual experiments the "straight" lines already referred to are definite and clear. However, it is obvious on reference to Table II that, in spite of the apparent regularity of the experiments as judged from the graphs, too much significance should not be attached to the values for k_1 calculated from the first "straight" line. My experience indicates that although it is relatively simple to obtain check results for k_2 the same is not true for k_1. It is this observation in particular which forces the conclusion that the "straight" line in the initial part of the reaction is probably illusory.

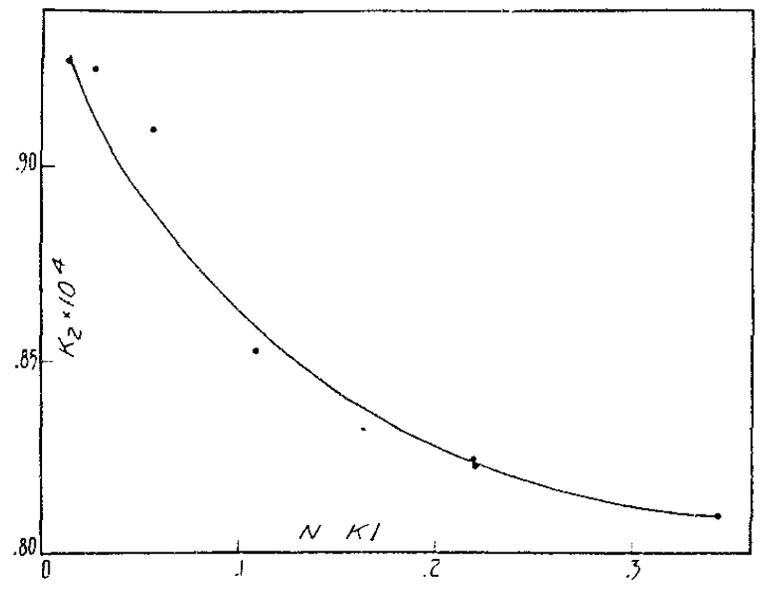


FIG. 2

It is further evident from Table II that there is a regular variation of k_2 with concentration of potassium iodide. As the concentration of potassium iodide increases, values of k_2, the velocity constant for the second part of the reaction, decrease. This result is in qualitative agreement with the observations of Brönsted and King[1] and of Kilpatrick[2] on the "secondary kinetic salt effect" in a hydroxyl ion catalyzed reaction in phosphate buffer.[3] The variation of k_2 with concentration of potassium iodide is plotted in Fig. 2. The results obtained indicate definitely that I^- ion is not catalytically active in this reaction.

In Table II the values listed under I_1 indicate the approximate decrease in molarity of iodine in the reaction mixture when the first cloudiness was observed in the solutions. This cloudiness is due to the precipitation of iodoform. The time when this cloudiness was first noted was recorded for each experiment. From this data it was possible to calculate approximately the amount of iodine which disappeared before any iodoform precipitated. Those places marked "n" indicate that in those reactions no precipitation of iodoform was observed. It is noteworthy that increase in concentration delays the precipitation of iodoform although it affects the shape of the reaction curve

[1] Brönsted and King: J. Am. Chem. Soc., **47**, 2523 (1925).
[2] Kilpatrick: J. Am. Chem. Soc., **48**, 2091 (1926).
[3] Brönsted and Teeter: J. Phys. Chem., **28**, 579 (1924); Brönsted and King: loc. cit.

not at all. The location of the point where the first "straight" line cuts the second "straight" line (called here the "break-point") is likewise but slightly affected by variation in concentration of potassium iodide. Precipitation of iodoform occurred always after the "break-point." This point will be referred to later.

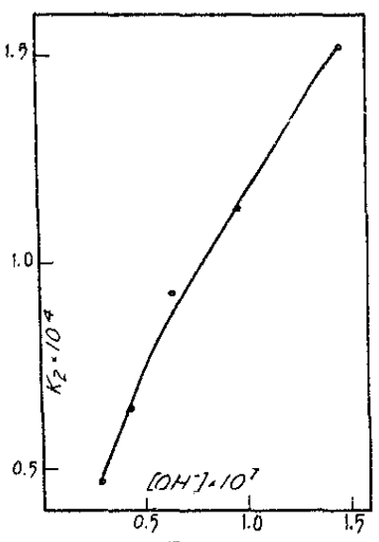


FIG. 3

Table III reviews the variation of the velocity constant, k_2, with hydrogen ion concentration and with hydroxyl ion concentration (which is equal to $10^{-14}/[H^+]$). The results are plotted in Fig. 3. Values for I_1 are also given.

Theoretical. The mathematical unravelment of the reactions involved is an impossibility with the data at hand. There are probably reactions involving simultaneous and successive formation of mono-iodoacetone, di-iodoacetone, tri-iodoacetone, and iodoform. The concentrations of these substances together with those of acetone, iodine, hydroxyl ion (presumably a constant in buffer solution), hydrogen ion, iodide ion, and triiodide ion may be designated as variable factors. The effect of hydrogen ion is negligible at the concentrations at which it exists in alkaline solution. The results given in Table II likewise indicate that, for the low concentrations of iodine and potassium iodide in the reaction mixtures, iodide and triiodide ions also have a negligible effect. The point has previously been made that the liberation of hydrogen ion during the course of the experiment has no effect on the concentration of hydroxyl ion since any hydrogen ion formed is taken up by the buffer. This, of course, is not wholly true. It is possible that during the second part of the reaction there is a tendency toward constant "speeding up" due to the liberation of some autocatalyst but that this effect is neutralized because of the slow simultaneous removal of hydroxyl ion which is also a catalyst for the reaction. It should be noted here that in all the experiments reported the total molarity of hydrogen ion liberated at the end of the reaction was less than one twelfth of the molarity of the buffer salts—a ratio small but not negligible. The variation in concentration of acetone is insignificant.

TABLE III

Effect of Variation of Hydrogen and Hydroxyl Ion Concentrations on Reaction Velocity Constant, k_2, in Phosphate Buffer.

Exp.	P_H	$[H^+] \times 10^7$	$[OH^-] \times 10^7$	$k_2 \times 10^4$	I_1
159	6.468	3.40	0.294	0.470	0.0017
156	6.643	2.28	.439	.647	——
154d	6.813	1.56	.641	.924	.0015
155	6.979	1.02	.980	1.129	.0012
160	7.168	.679	1.473	1.521	.0012

It can be shown that because there are apparently a few successive reactions it is necessary to know the initial velocity of disappearance of iodine in order to obtain any information as to the values of the several velocity constants of the reactions involved. It has been previously pointed out, however, that it was impossible to measure the rate of the reaction in the initial part since the solution of the small quantity of acetone used raised the temperature of the mixture; it was necessary to wait at least fifteen minutes for the reaction mixture to reach the temperature of the thermostat before the rate of reaction could be studied.

The objection may be made that the peculiar nature of the results obtained may be attributed to the method of titration employed. Speed of titration is an important factor. An indication of the speed with which these titrations were made may be drawn from the fact that it was common practice to remove a sample from the thermostat, titrate it with thiosulfate, weigh the burette, and remove another sample from the thermostat ready for titration all within four minutes. With such speeds little trouble is encountered due to "fading" of the end-point. The serious objection may be made that at the pH values employed there was no justification for the use of sodium thiosulfate since in alkaline solution sulfate as well as tetrathionate is formed by the reaction of thiosulfate with iodine. Kolthoff[1] found that a solution of pH less than 6.5 must be used in titrating 0.01 *N* iodine and that for 0.001 *N* iodine the pH should be less than 5. However, the error is of a nature which will affect not the shapes of the curves but only the slopes of the "straight" lines.

The possibility that iodoform may be a catalyst for the reaction is suggested by the fact that the "break-point" already referred to occurs just before the precipitation of iodoform; the idea is suggested that when the iodoform attains the constant concentration corresponding to its solubility the reaction attains maximum and constant speed. In direct test of this theory an attempt was made to study the effect of iodoform dissolved in the reaction mixture. Vulpius[2] reports that 0.106 g of iodoform dissolve in a liter of water. Judging from the difficulty of solution of the iodoform (0.1 g were never dissolved in a liter of water no matter what means was used) the author is of the opinion that the value reported for the solubility of iodoform in water is much too high. In testing the catalytic activity of iodoform, many precautions were taken to insure saturation of the solution; nevertheless, the initial speed was never increased nor was precipitation of iodoform observed in any of the experiments until the usual time after the "break-point" which was never appreciably shifted. In this connection it is well to remember that although the character "break-point" was observed in solutions containing high concentrations of potassium iodide no precipitation of iodoform was observed even on long standing or after prolonged shaking although its odor was pronounced.

Temperature Coefficient. Rice[3] reported that I measured the value of k_{35}/k_{25} for the reaction between acetone and iodine when catalyzed by an

[1] Kolthoff: Z. anal. Chem., **60**, 338 (1921).
[2] Vulpius: Pharm. Centralbl., **34**, 117 (1893).
[3] Rice: J. Am. Chem. Soc., **45**, 2808 (1923).

alkaline buffer solution and found it to be 2.52. In the experiment referred to, I employed the "two-thermostat" method[1] and compared the velocities of the initial "straight" lines. In the light of later knowledge I came to the conclusion that the method was subject to two criticisms for this reaction: (1) I did not take into account the initial temperature effect due to the solution of acetone; (2) because of the anomalous results obtained with the initial straight lines they ought not to be compared directly.

In two experiments at pH 6.813 in phosphate buffer at 35° values of 3.34 and 3.38 $\times$ 10^{-4} were obtained for the velocity constant, k_2. Comparison of these values with that of 0.924 $\times$ 10^{-4} for equivalent salt concentration at 25° (see Table II) gives a value for k_{35}/k_{25} of 3.61 at pH 6.813 in phosphate buffer. This is somewhat higher than for the hydrogen ion catalyzed reaction, a result contrary to that expected from the protion theory of catalysis.[2]

Catalysis near the Catalytic Minimum Point

The range of hydrogen ion concentrations from pH 3.04 to pH 6.31 is adequately covered by Walpole's sodium acetate-acetic acid and sodium acetate-hydrochloric acid standard buffer solutions.[3] The iodine-acetone reaction was studied colorimetrically in such solutions in the following way. To a number of 100 cc volumetric flasks containing solutions of buffers which would give exactly known concentrations of hydrogen ion when the flasks were filled to the mark were added about 2 cc of starch solution each and exactly equal volumes of acetone measured out from a pipette. The flasks were filled almost to the mark and placed in the thermostat to attain temperature. After the lapse of about twenty minutes they were removed singly; equal volumes of iodine solution of fixed concentration were added from a pipette; the time was noted as initial when the iodine solution began to run in; and the flasks were quickly filled to the mark, shaken, and returned to the thermostat. The time when the iodine-starch blue color just disappeared was noted as final time for each bottle. The difference in times was the time recorded for the reaction. The catalytic minimum point reported is the pH determined graphically at which maximum time is required for the disappearance of the blue color. In order to obviate error sodium acetate solutions made up in several different ways were used. The same precautions were taken with the acetic acid and hydrochloric acid solutions. In some experiments in order to eliminate the possible effects of starch, solutions of the latter were added just before completion of the reaction. In all cases practically the same values were obtained for the catalytic minimum point. Further to ensure the accuracy of the method blanks were made up containing no acetone. The blue color remained unchanged in one such bottle after the lapse of a year whereas with acetone present it would disappear in about an hour.

Three experiments in acetic acid-sodium acetate buffer at 25° yielded pH values for the catalytic minimum point of 3.8, 3.8, and 3.87. At 40° pH values of

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[1] Rice and Kilpatrick: loc. cit.

[2] Rice: loc. cit.

[3] Walpole: J. Chem. Soc., **105**, 2501 (1914).

3.82 and 3.84 were obtained. In hydrochloric acid-sodium acetate buffer at 25° the catalytic minimum point was found to be at pH 3.95. The mean of these values is pH 3.85, and it is obvious that neither for a temperature variation of 15° nor for a change in the buffer salt does the catalytic minimum point vary much from this value. This value is of an order ten times as great as that obtained by extrapolation in studying the autocatalyzed reaction.[1]

Part of this shift may be explained on the following reasoning. The term dx/dt in the autocatalytic equation,[2] $dx/dt = (a - x)\{k_H(c + x) - k_{OH}d\}$, although measured by disappearance of I_2 does not represent the rate of this disappearance but the rate of the initial iodine-acetone reaction. The hydroxyl ion has only its normal or non-specific influence on this reaction but is apparently solely responsible for the succeeding reactions in which more iodine is removed practically instantaneously with the eventual formation of iodoform. The effect of these reactions is by liberation of more hydrogen ion to bring the reaction more rapidly to the catalytic minimum point. This point is unchanged for the primary reaction itself. At this point its velocity is a minimum and on the acid side of it its velocity again increases although the velocity of the second reactions (forming di-iodoacetone, etc.) rapidly falls off to an infinitesimal of another order. In the buffer solution method for determining the catalytic minimum point, the rate measured is that of disappearance of iodine. Because it catalyzes the secondary reactions, the hydroxyl ion is more active in effecting this disappearance of iodine than is hydrogen ion at the true catalytic minimum point. The apparent catalytic minimum point is consequently shifted toward the acid side. The shift observed is at least two and a half times as great as can be accounted for on this basis. It may help to recall, however, that in phosphate buffers an apparent autocatalytic action was observed. There are, therefore, other catalysts for the iodine-acetone reactions and it may be the presence or generation of one of these in buffers which may account for the entire shift. For the iodine-acetone reaction the method of extrapolation offers the more trustworthy means for determination of the true catalytic minimum point.

Summary

1. The reactions between iodine and acetone have been studied in the vicinity of pH 7 and of the catalytic minimum point in buffer solution.

2. The reactions are complicated and the nature of the catalysts has not been fully established.

3. There is an approximately linear relationship between the velocity of the reactions in their later stages and the hydroxyl ion concentration near pH 7.

4. The temperature coefficient k_{35}/k_{25} for the second stage of this reaction at pH 6.813 in phosphate buffer has been determined to be 3.61. This is not in conformance with the protion theory of catalysis.

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[1] Bergstein and Kilpatrick: loc. cit.

[2] Bergstein and Kilpatrick: loc. cit.

5. The apparent catalytic minimum point of this reaction has been found to be at pH 3.85 in acetate buffers. This figure is unchanged by a temperature variation from 25° to 40°.

The author wishes to express his appreciation to Professor F. O. Rice of Johns Hopkins University who directed the experimental work reported.

Photion Instrument Corporation,
409 E. 139 Street,
New York City.

-59

STUDIES IN ADSORPTION. PART XVII

Influence of Concentration of a Sol on its Coagulation by Electrolytes

BY S. GHOSH AND N. R. DHAR

In several papers[1] published from this laboratory the influence of change of concentration of a sol on its coagulation by electrolytes has been studied. It has been shown that, in general, the dilution rule, viz. the greater the concentration of a sol the greater is the amount of an electrolyte necessary for coagulation, is valid for those sols, which are not capable of adsorbing appreciably the ions carrying the same charge as the sol from the coagulating electrolytes. On the other hand, those sols, which appreciably adsorb ions carrying the same charge as the sol, do not follow the general dilution rule when coagulated by monovalent precipitating ions. In previous papers the general dilution rule has been found to be applicable to the sols of ferric hydroxide (positive and negative), chromium hydroxide (positive and negative), and stannic hydroxide (negative), whilst the rule is not applicable to the sols of arsenious sulphide, antimony sulphide, mastic and prussian blue.

In the present paper we have extended our investigations on the influence of concentration of the sols of antimony sulphide, stannic hydroxide and (positive) manganese dioxide (positive and negative), aluminium hydroxide, thorium hydroxide, vanadium pentoxide, prussian blue, uranium ferrocyanide, gum dammar, gamboge, sulphur (Weimarn), gold and silver, towards their coagulation by various electrolytes.

We have also determined the adsorption of both positive and negative ions from an electrolyte by a positively charged sol of manganese dioxide as well as by freshly precipitated manganese dioxide, and we have shown that our results on adsorption support our views based on the phenomenon of adsorption to explain the abnormal behaviour of a sol on dilution.

Antimony Sulphide Sol

We have already shown that both arsenious sulphide and antimony sulphide sols behave abnormally towards dilution when coagulated by KCl, NaCl, KNO_3, etc., because these sols are capable of adsorbing appreciable quantities of similarly charged Cl', NO'_3 ions, etc., from these electrolytes. We have however, shown with a sol of arsenious sulphide that this sol behaves normally towards dilution when coagulated by salts like $AgNO_3$, methyl violet, quinine hydrochloride, strychnine hydrochloride, etc. This is because as we have already indicated, the cations from $AgNO'_3$, methyl violet, quinine hydrochloride, strychnine hydrochloride, etc., are highly adsorbed in comparison with anions. In Table I the results are given as obtained by us when antimony sulphide sol is coagulated by these electrolytes:—

[1] J. Phys. Chem., **26**, 701 (1922); **28**, 313 (1924); **29**, 435, 659 (1925); Kolloid-Z., **34**, 262 (1924); **36**, 129, (1925).

TABLE I

Coagulation of antimony sulphide sol by alkalids, dyes, etc.
Concentration of the sol = 0.54 grms. Sb_2S_3 per litre.
5 c.c. of the sol made up to 10 c.c. = Sol A.
Volume = 10 c.c.; time = ½ hour.

Electrolyte	Amount to coagulate in c.c. Sol A	Sol A/2	Sol A/4
$AgNO_3$ M/6.25	0.6	0.45	0.30
Quinine hydrochloride M/2160	0.40	0.20	0.15
Strychnine hydrochloride M/1210	1.45	0.95	0.70
Methylene blue M/1832	3.50	1.80	1.00
$[Co(NH_4)_4CO_2]\ NO_3$ M/1320	2.05	1.60	1.10

It will be seen from Table I that when antimony sulphide sol is coagulated by $AgNO_3$, quinine hydrochloride, strychnine hydrochloride, and methylene blue, the general dilution rule, viz., the greater the concentration of a sol the greater is the amount of an electrolyte necessary to coagulate it, is strictly followed with these electrolytes. These results are exactly similar to those obtained by us on the coagulation of arsenious sulphide sol by these electrolytes. The normal behaviour of antimony sulphide sol towards dilution when coagulated by either $AgNO_3$ or dyes and alkaloids is certainly due to very high adsorption of the cations in comparison with that of anions from these electrolytes. Antimony sulphide sol also behaves normally towards dilution when coagulated by an univalent cobalt ammine $[Co(NH_4)_4\ CO_3]NO_3$, because the cation having a large molecular weight is highly adsorbed by the sol.

Stannic Hydroxide Sol (positive)

A positively charged stannic hydroxide sol has been prepared by adding a dilute solution of caustic soda to a solution of stannic chloride in presence of small quantities of ferric chloride, till a precipitate just begins to form. The sol thus prepared is dialysed for a week to free it from electrolytes and was stored in a Jena glass flask. The sol thus prepared and dialysed is highly sensitive towards electrolytes and the coagulation experiments with this sol has to be finished in two days, otherwise the sol coagulates on standing. Table II shows the results obtained in the coagulation of this sol at different concentrations by various electrolytes:—

TABLE II

Concentration of the sol = 3.52 grams SnO_2 per litre
Sol A = 4 c.c. of the original sol made up to 10 c.c.
Volume = 10 c.c.; Time = 1 hour.

Electrolyte		Amount to coagulate in c.c. Sol A	Sol A/2	Sol A/4
KBr	N/500	4.0	2.15	1.00
KCl	N/500	4.5	1.90	1.00
K_2SO_4	N/4000	3.3	1.20	0.50

The foregoing results show that the sol is very unstable towards electrolytes and behaves quite normally towards dilution when coagulated by monovalent and bivalent anions.

Manganese Dioxide Sol (negative)

This sol is obtained by treating a dilute solution of potassium permanganate with a dilute solution of hydrogen peroxide according to the method of Bredig and Marck.[1] The sol thus obtained is negatively charged and contains free alkali, which is obtained as the result of the reaction. It has been observed that the sol of a deep brown colour is less stable than that which has a reddish tinge due to the adsorption of permanganate ion, which certainly stabilises the sol. The manganese dioxide sol of a reddish brown colour was prepared and dialysed for about a week when it was free from alkali.

The coagulation of the negatively charged manganese dioxide sol has been investigated by Bredig and Marck,[1] Ganguly and Dhar.[2] Ganguly and Dhar used a sol containing gelatine and, therefore, the sol was not pure. In this paper we have carefully studied the coagulation of this sol purified by dialysis at different dilutions.

In Table III the results are reproduced:

TABLE III

Concentration of the sol = 0.80 grm. MnO_2 per litre.
2 c.c. of the sol made up to 8 c.c.
Volume = 8 c.c.; Time = 1 hour.

Electrolyte	Concentration	Amount added in c.c.	Precipitating concentration
KCl	N/20	1.15	0.00719
KBr	N/20	1.15	0.00719
KI	N/20	1.20	0.00750
K_2SO_4	N/20	1.25	0.00781
KNO_3	N/20	1.00	0.00625
KOH	N/20	2.80	0.01750
NaCl	N/20	1.35	0.00844
HCl	N/20	0.55	0.00344
$AgNO_3$	N/100	0.72	0.00090
$BaCl_2$	N/500	0.80	0.00020
$MgCl_2$	N/500	1.25	0.00031
$MgSO_4$	N/500	1.25	0.00031
$CuSO_4$	N/500	1.05	0.00026
$Al(NO_3)_3$	N/1000	2.40	0.00030
$Th(NO_3)_4$	N/1000	1.30	0.00016

[1] "Van Bemmelen Gedenkboek," 342 (1910).
[2] J. Phys. Chem., **26**, 701 (1922).

An examination of Table III gives the following order for the precipitation values, beginning with the highest one: KOH > NaCl > K_2SO_4 > KI > KCl, KBr > KNO_3 > HCl > $AgNO_3$ > $MgCl_2$, $MgSO_4$ > $Al(NO_3)_3$ > $CuSO_4$ > $BaCl_2$ > $Th(NO_3)_4$.

From the experimental results, it appears that the Schulze-Hardy law is applicable to this sol with the exception of $Al^{'''}$ ion, which possesses a higher precipitation value than either of the bivalent ion $Ba^{''}$ or $Cu^{''}$. Moreover, of all the monovalent cations, $Ag^{'}$ ion possesses the greatest coagulating power. It is well-known that $Ag^{'}$ ions are highly adsorbed by MnO_2[1].

Table IV will show the effect of anions on the coagulation of negatively charged manganese dioxide sol.

TABLE IV

Electrolyte	Concentration	Amount added in c.c.	Precipitating concentration
KCl	N/20	1.15	0.00719
KBr	N/20	1.15	0.00719
KI	N/20	1.20	0.00750
KNO_3	N/20	1.00	0.00625
K_2SO_4	N/20	1.25	0.00781
KOH	N/20	2.80	0.01750

The precipitation values of different salts with the same cation $K^{'}$ is in the following order, beginning with the highest one KOH > K_2SO_4 > KI > KCl, KBr > KNO_3. The sol is about two and a half times more stable towards KOH than towards KCl. This shows that $OH^{'}$ ions are appreciably adsorbed by manganese dioxide, as has been experimentally shown by Chatterji and Dhar.

Table V shows the influence of change in the concentration of the sol towards its coagulation by various electrolytes:—

TABLE V

Concentration of the sol = 0.80 grm. MnO_2 per litre.
Sol A = 2 c.c. of the sol made up to 8 c.c.
Volume = 8 c.c.; Time = 1 hour.

Electrolyte		Amount to coagulate in c.c. Sol 2 A	Sol A	Sol A/2
KCl	N/20	1.30	1.15	1.00
K_2SO_4	N/20	1.35	1.25	1.10
KOH	N/20	2.80	2.80	2.70
$AgNO_3$	N/100	1.35	0.72	0.55
$BaCl_2$	N/500	1.20	0.80	0.45
$Al(NO_3)_3$	N/1000	>4.00	2.40	1.30
$Th(NO_3)_4$	N/1000	2.75	1.30	0.65

[1] Compare Chatterji and Dhar: Kolloid-Z., **33**, 18 (1923).

It is obvious from our experimental results that the sol behaves normally on dilution towards all electrolytes (that is the greater the concentration of the sol the greater is the amount of an electrolyte necessary to coagulate the sol) except with KOH, the amount of which is practically constant for all the dilutions of the sol. We have shown that abnormality of a sol towards its dilution is intimately connected with the adsorption of the ion carrying the same charge as the sol. The tendency of KOH to behave abnormally on diluting manganese dioxide sol is, therefore, a direct consequence of the adsorption by OH' ions by the negatively charged manganese dioxide sol.

Positively Charged Manganese Dioxide Sol

When negatively charged manganese dioxide sol is coagulated by polyvalent cations like $Fe^{'''}$, $Al^{'''}$, $Th^{''''}$, etc., it is observed that very small amounts of these cations are necessary to coagulate a given amount of the sol. If, however, greater quantities of these coagulating ions are added all at once, we have observed that coagulation does not occur and charge reversal takes place, the sol now moving to the cathode in an electric field.

A positively charged manganese dioxide sol is prepared by adding N/10 $FeCl_3$ solution to a litre of the negatively charged sol. The sol is of deep brown colour with a reddish tinge and is fairly stable. In order to free the sol from an excess of $FeCl_3$, it was dialysed for a week, when the filtrate obtained by coagulating the sol did not show any test for $Fe^{'''}$ ion. The results on the coagulation of this sol by a few selected electrolytes throw considerable light on the phenomenon of coagulation and are given in Table VI.

TABLE VI

Concentration of the sol = 0.92 grm. MnO_2 per litre
2 c.c. sol made up to 8 c.c.
Volume = 8 c.c.; Time = 1 hour

Electrolyte	Concentration	Amount added in c.c.	Precipitation value
KCl	N/20	1.8	0.01125
$CuCl_2$	N/1	0.65	0.08125
KBr	N/20	1.75	0.01094
KNO_3	N/20	1.60	0.01000
$AgNO_3$	N/2.725	1.20	0.05505
K_2SO_4	N/1000	0.80	0.00010
$MgSO_4$	N/1000	0.90	0.00011
$CuSO_4$	N/500	0.95	0.00024
$KMnO_4$	N/400	0.55	0.00017

The following order is obtained from Table VI, beginning with the electrolyte possessing the greatest precipitation value:—

$CuCl_2 > AgNO_3 > KCl > KBr > KNO_3 > CuSO_4 > KMnO_4 > MgSO_4 > K_2SO_4$.

The sol being positively charged, it is evident that anions are the chief coagulating ions. An examination of Table VI reveals the fact that far greater

quantities of copper chloride, silver nitrate, etc., are necessary for coagulation than those of KCl, KNO_3, etc. This peculiar behaviour is certainly to be ascribed to the greater adsorption of cations like $Cu^{\cdot\cdot}$ or $Ag^{\cdot}$ than that of $K^{\cdot}$ by MnO_2, so that the sol is partially stabilised by the adsorption of $Cu^{\cdot\cdot}$ or $Ag^{\cdot}$ ions and more of an anion is necessary to coagulate the sol. It has already been shown in publications from this laboratory that manganese dioxide highly adsorbs copper or silver ions.[1] It is also seen from the above order of precipitation values that MnO_4' ion from $KMnO_4$ is as good a coagulating ion as the bivalent ion SO_4''. We have already observed that permanganate ions are highly adsorbed by manganese dioxide and stabilise the negatively charged manganese dioxide sol; and consequently, a greater concentration of $KMnO_4$ is necessary to coagulate the negatively charged sol than that of KCl or NaCl.

Table VII the influence of change of concentration of manganese dioxide sol (positively charged) on its coagulation by various electrolytes has been studied.

TABLE VII

Concentration of the sol = 0.92 grm MnO_2 per litre.
Sol A = 2 c.c. sol made up to 8 c.c.
Volume = 8 c.c.; Time = 1 hour

Electrolyte		Amount to coagulate in c.c.		
		Sol 2 A	Sol A	Sol A/2
KCl	N/20	2.0	1.80	1.60
$CuCl_2$	N	0.55	0.65	0.75
KBr	N/20	2.0	1.75	1.60
KNO_3	N/20	1.6	1.4	1.0
$AgNO_3$	N/2.725	1.1	1.2	1.3
K_2SO_4	N/1000	1.35	0.8	0.5
$MgSO_4$	N/1000	1.55	0.9	0.65
$CuSO_4$	N/500	1.0	0.95	0.80
$KMnO_4$	N/400	1.10	0.55	0.25

The results in Table VII reveal some very interesting facts on the coagulation of sols. It will be seen that the general dilution rule that the greater the concentration of the sol the greater is the amount of the coagulating ion necessary for coagulation is applicable for the anions Cl' and NO'_3, when electrolytes like KCl and KNO_3 are used. On the other hand, the general dilution rule is not applicable to these anions (Cl' and NO_3') when electrolytes like $CuCl_2$ and $AgNO_3$ are used. The fact that more of $ClCu_2$ or $AgNO_3$ is required to coagulate the dilute sol than a concentrated one, is evidently due to the high preferential adsorption of $Ag^{\cdot}$ and $Cu^{\cdot\cdot}$ ions by manganese dioxide.

[1] Compare Chatterji and Dhar: loc. cit.

Adsorption of Positive and Negative Ions of Electrolytes by Manganese Dioxide.

When small amounts of cupric chloride are added to a positively charged manganese dioxide sol it will attract and adsorb the cupric ions because of the chemical affinity of manganese dioxide for cupric ions. If, however, larger quantities of cupric chloride are added, the adsorption of chlorine ions becomes greater than that of cupric ions, and the sol is actually coagulated by a concentrated solution of this electrolyte. Now, I have already shown, that the abnormal behaviour of a sol on dilution towards its coagulation by an electrolyte, is due to the preferential adsorption of similarly charged ions by the sol, and that the ratio of the amount of adsorption of ions bearing the same charge as the sol to that of the ion of opposite charge should increase as the sol is diluted. In Table VIII our results on the adsorption of cupric and chlorine ions by positively charged manganese dioxide sol as well as by freshly precipitated manganese dioxide are recorded:—

TABLE VIII

Adsorption of $Cu^{\cdot\cdot}$ and Cl' ions from a solution of $CuCl_2$ by positively charged manganese dioxide sol.

Concentration of the sol = 0.320 grms. MnO_2 per litre.

Sol A = 20 c.c. of the sol made up to 50 c.c.

Volume = 50 c.c.; Time = 20 hours

Concentration of the sol	Original concentration in millimoles	Final concentration in millimoles	Adsorption in millimoles	R[1]
A	5.00 $Cu^{\cdot\cdot}$	4.9958 $Cu^{\cdot\cdot}$	0.0042 $Cu^{\cdot\cdot}$	0.092
	10.00 Cl'	4.9544 Cl'	0.0456 Cl'	
A/2	5.00 $Cu^{\cdot\cdot}$	4.9975 $Cu^{\cdot\cdot}$	0.0025 $Cu^{\cdot\cdot}$	0.109
	10.00 Cl'	9.9771 Cl'	0.0229 Cl'	

(The results given are the mean of two experiments).

Hence the ratio of the amount of adsorption of cupric ion to that of chlorine ion is greater with the sol A/2 than that observed with the sol A.

In Table IX the results are given as obtained by us on the adsorption of both cupric ion and chlorine ion from a copper chloride solution by freshly precipitated manganese dioxide prepared after the method of Sarkar and Dhar.[1]

TABLE IX

Sample of manganese dioxide contains 74% MnO_2 and 26% water

Volume = 50 c.c.; Time = 20 hours

Amount of the adsorbent in grm.	Original concentration in millimoles	Final concentration in millimoles	Adsorption in millimoles	R
1.0	20.00 $Cu^{\cdot\cdot}$	12.47 $Cu^{\cdot\cdot}$	0.3765 $Cu^{\cdot\cdot}$	2.27
	40.00 Cl'	36.68 Cl'	0.1660 Cl'	
0.5	20.00 $Cu^{\cdot\cdot}$	14.71 $Cu^{\cdot\cdot}$	0.2645 $Cu^{\cdot\cdot}$	3.07
	40.00 Cl'	38.34 Cl'	0.0830 Cl'	
0.25	20.00 $Cu^{\cdot\cdot}$	17.06 $Cu^{\cdot\cdot}$	0.1470 $Cu^{\cdot\cdot}$	3.54
	40.00 Cl'	39.17 Cl'	0.0415 Cl'	

R is the ratio of the amounts of adsorption of cupric ion to that of chlorine ion.

[1] Z. anorg. Chem., **121**, 135 (1922).

The results on the adsorption of both cation and anion from a copper chloride solution by freshly precipitated manganese dioxide also show, that the ratio of the amounts of adsorption of the cation to that of the anion increases as the amounts of the adsorbent used are decreased. These results are exactly similar to those obtained by us with positively charged manganese dioxide sol, and greatly strengthen our views already discussed in order to explain the abnormal behaviour of many sols on dilution, viz. more of an electrolyte is necessary to coagulate a dilute sol than a concentrated one.

From Table VIII it will be seen that the amount of adsorption of cupric ion by sol A/2 is greater than half the amount of adsorption of the same ion with sol A. This is because, as is well-known, the adsorption of a substance is always greater per unit mass of the adsorbent when smaller amounts of the adsorbent are used. On the other hand, the amount of adsorption of chlorine ions, which is necessarily due to the charge neutralisation of the colloid particles, is exactly halved when the sol is diluted twice.

It has been shown by Chatterji and Dhar that freshly precipitated manganese dioxide mainly adsorbs the cations from electrolytes, leaving the solution acidic. This is because manganese dioxide being acidic in nature attracts and adsorbs the cation from an added electrolyte, leaving the anion in the solution free where it finds its counterpart $H^{\cdot}$ ion from water, and, therefore, gives out acid. It is, therefore, obvious that the amount of an acid liberated during the adsorption of an electrolyte by manganese dioxide, measures the excess of anions, which are not adsorbed by it. Hence, if the cations are only adsorbed by manganese dioxide from an added electrolyte, it is expected that the amount of the acid set free will be equivalent to the amount of cations adsorbed. But as a matter of fact, experimental results prove that the amount of the acid set free is less than the amount which is equivalent to the adsorption of cations. This is because, when the electric charge on manganese dioxide has sufficiently increased due to a high preferential adsorption of cations only, the anions which are also present will be attracted due to electrical attraction by the positively charged surface and will be adsorbed. In other words, the number of anions which can remain free in the solution are smaller than the amount which is equivalent to the amount of cations adsorbed. Hence, it is evident that the amount of adsorption of anions can be easily determined by subtracting the amount of the acid actually liberated from the amount of acid equivalent to the amount of cations adsorbed.

In Table X the amount of adsorption of cations by freshly precipitated manganese dioxide has been determined directly and the amount of adsorption of anions has been calculated from the amount of the acid actually set free, when electrolytes like $AgNO_3$, $CuCl_2$, etc, are added to manganese dioxide:—

TABLE X

Adsorption of $AgNO_3$ and $CuCl_2$ by manganese dioxide

Initial concentration	Amount of adsorbent in gram.	Amount of cation adsorbed in gram.	Amount of acid liberated per gram.	Amount of anion adsorbed in millimoles per gram.	R
		Electrolyte $AgNO_3$			
2N	0.5	4.256	2.036	2.220	1.917
"	1.0	4.200	1.936	2.264	1.813
"	1.5	4.119	1.332	2.787	1.478
"	2.0	4.097	1.200	2.897	1.414
0.5N	0.5	2.297	1.528	0.769	2.987
"	1.0	2.277	1.251	1.026	2.219
"	1.5	2.259	0.948	1.311	1.723
"	2.0	2.456	1.000	1.456	1.689
		Electrolyte $CuCl_2$			
2N	0.5	1.297	0.480	0.817	1.587
"	1.0	1.284	0.391	0.893	1.438

The results in Table X prove that for the electrolytes $AgNO_3$ and $CuCl_2$ the ratio of the amount of adsorption of the cation to that of the anion, increases as the amount of the adsorbent used is decreased I have already shown that negatively charged manganese dioxide sol behaves normally towards dilution when coagulated by silver nitrate or a cupric salt. On the other hand, positively charged manganese dioxide sol behaves abnormally towards dilution when coagulated by these electrolytes.

Hence the foregoing experimental results on the adsorption of anions and cations by manganese dioxide sol as well as by precipitated manganese dioxide are in line with those obtained with arsenious sulphide and potassium chloride and strongly support our explanation of the abnormal behaviour of sols on dilution towards their coagulation by univalent ions.

Aluminium Hydroxide Sol

The coagulation of aluminium hydroxide sol has been investigated by Gann,[1] Ishizaka,[2] and Weiser and Middleton.[3] The influence of change of concentration of this sol towards its coagulation by various electrolytes has not been studied before and, therefore, this has been investigated by us.

A sol of aluminum hydroxide is prepared by precipitating $Al(OH)_3$ from a solution of $Al(NO_3)_3$ by ammonia at the ordinary temperature and washing the precipitate free of electrolytes by decantation. It is observed that when the washing has been continued sufficiently long, the precipitated aluminium hydroxide gradually passes into the colloidal state and finally a fairly stable but dilute sol of $Al(OH)_3$ can be obtained. The sol thus obtained is positively charged.

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[1] Kolloidchem. Beihefte, **8**, 125 (1916).
[2] Z. physik. Chem., **83**, 97 (1913).
[3] J. Phys. Chem., **24**, 630 (1920).

In Table XI the results are given as obtained by us on the coagulation of aluminium hydroxide sol at different dilutions by various electrolytes:—

TABLE XI

Concentration of the sol = 0.60 grm. Al_2O_3 per litre
Sol A = 2 c.c. of the sol made up to 6 c.c.
Volume = 6 c.c.; Time = 1 hour

Electrolyte	Amount to coagulate in c.c. Sol 2A	Sol A	Sol A/2
KCl N/10	1.75	1.50	1.30
$K_2C_2O_4$ N/400	1.65	1.25	0.80
K_2SO_4 N/400	1.50	0.65	0.45
K_3Cit N/2,000	1.30	0.65	0.30
$K_3Fe(CN)_6$ N/2,000	1.80	1.25	0.95
$K_4Fe(CN)_6$ N/2,500	1.80	0.90	0.45

The sol being positively charged the anions possess the coagulating effect.

The foregoing results conclusively prove that the greater the concentration of the sol the greater is the amount of an electrolyte necessary to coagulate it irrespective of the valency of the coagulating ion. Similar results have been recently obtained by Sen[1] with a suspension of aluminium hydroxide stabilised by different organic acids.

We have already shown with $Fe(OH)_3$ sol that it obeys the general dilution rule when coagulated by electrolytes like KCl, K_2SO_4, $K_4Fe(CN)_6$, etc., but behaves abnormally on dilution when coagulated by HCl, $FeCl_3$, $Al(NO_3)_3$, etc., as appreciable amounts of cations are adsorbed by ferric hydroxide from these electrolytes. It is, therefore, expected that $Al(OH)_3$ sol, which is also known to adsorb cations from electrolytes like HCl, $FeCl_3$, $Al(NO_3)_3$, etc., appreciably, should behave abnormally on dilution when coagulated by these electrolytes, but as these electrolytes possess a solvent action and appreciably dissolve $Al(OH)_3$ sol at their precipitating concentrations the investigations from this point of view could not be pursued.

Vanadium Pentoxide Sol

Vanadium pentoxide sol is prepared after the method of Biltz[2] and is dialysed for a week, when it is free from hydrochloric acid. The sol is negatively charged. The coagulation of vanadium pentoxide sol has been investigated by Freundlich and Leonhardt[3], who have shown that the Schulze-Hardy law is applicable to this sol. In a recent paper Gessner[4] has studied the behaviour of vanadium pentoxide sol from various points of view, and his results on the precipitation values of NaCl and $CaCl_2$ for varying concentrations of vanadium pentoxide have been cited by Wiegner[5] to prove that this

[1] J. Phys. Chem., **28**, 1029 (1924).
[2] Ber., **37**, 1095 (1904).
[3] Kolloidchem. Beihefte, **7**, 195 (1915).
[4] Kolloidchem. Beihefte, **19**, 213 (1924).
[5] Kolloid-Z. (Zsigmondy Festschrift), **36**, 341 (1925).

sol becomes stable on dilution towards an univalent electrolyte like NaCl. Gessner has, however, used different samples of vanadium pentoxide sol in his experiments on the coagulation of this sol at different concentrations. Hence it is apparent that no definite conclusion can be drawn from the experiments of Gessner on the stability of the sol on dilution, for it is well-known that the coagulating power of an electrolyte is dependent on the mode of the preparation of a sol and it is different for different samples of a sol obtained from the same substance.

In Table XII our results are given with the same sample of the sol and shows the influence of change of concentration towards its coagulation by various electrolytes:—

TABLE XII

Concentration of vanadium pentoxide sol = 0.92 grm. V_2O_5 per litre
Sol A = 2 c.c. of the sol made up to 6 c.c.
Volume = 6 c.c.; Time = ½ hour

Electrolyte	Amount to coagulate in c.c.		
	Sol A	Sol A/2	Sol A/4
KCl N/10	0.80	0.80	0.70
NaCl N/10	2.05	1.90	1.85
$BaCl_2$ N/500	1.20	1.00	0.75
$Al(NO_3)_3$ N/1,000	1.80	0.95	0.55

The foregoing results are not in line with the conclusions of Wiegner, and prove that the general dilution rule is obeyed by this sol and more of an electrolyte is required to coagulate a concentrated sol than a dilute one irrespective of the valency of the coagulating ion.

We have observed that vanadium pentoxide sol appreciably adsorbs a cation from the coagulating electrolyte leaving the filtrate acid.

Thorium Hydroxide Sol

The sol is prepared after the method of Biltz, which consists in dialysing a solution of thorium nitrate. The thorium nitrate solution is dialysed for a week in a parchment bag, when the sol of thorium hydroxide formed by hydrolysis of the salt is practically free from electrolytes. The sol thus formed is, however, very stable and could not be coagulated by even 3N KCl. The sol is, however, easily coagulated by a solution of $KBrO_3$.

Table XIII results are given when this sol is coagulated at different dilutions by various electrolytes:—

TABLE XIII

Concentration of the sol = 1.36 grams. ThO_2 per litre
Sol A = 2 c.c. of the sol made up to 6 c.c.
Volume = 6 c.c.; Time = ½ hour

Electrolyte		Amount to coagulate in c.c.		
		Sol 3A/2	Sol A	Sol A/2
$KBrO_3$	N/2.4	2.80	2.60	2.10
K_2SO_4	N/500	3.0	2.40	1.65
$K_4Fe(CN)_6$	N/1,000	3.60	2.70	1.40

The results in Table XIII show that thorium hydroxide sol behaves normally on dilution, when coagulated by monovalent, bivalent or polyvalent anions. The sol being positively charged the anions possess the coagulating effect.

Prussian Blue Sol

In a previous paper we have investigated the influence of dilution of prussian blue sol on its coagu tion by electrolytes and we have found that the sol behaves abnormally toward dilution when coagulated by KCl. Weiser and Nicholas have, however, reported that this sol behaves normally towards dilution when coagulated by KCl. Our sol was completely free from $K_4Fe(CN)_6$, whilst the sol used by Weiser and Nicholas contained some free $K_4Fe(CN)_6$. We have, therefore, made some experiments on the coagulation of prussian blue sol with KCl in the presence of $K_4Fe(CN)_6$. The results are given in Table XIV.

TABLE XIV

Concentration of the sol = 2.76 grms. prussian blue per litre
Sol A = 1 c.c. made up to 10 c.c.
Volume = 10 c.c.; Time = 20 hours

Concentration of the sol	Amount of $K_4Fe(ON)_6N/2$ added in c.c.	Amount of KClN/4. to coagulate in c.c
A	0.50	2.6
A/2	0.25	3.1
A/5	0.10	3.5

It is obvious from Table XIV that more abnormality towards dilution is observed with prussian blue sol when coagulated by KCl in the presence of $K_4Fe(CN)_6$. These results are very interesting and will be discussed in a subsequent paper.

Uranium Ferrocyanide Sol

This sol has never been studied before. We have prepared the sol of uranium ferrocyanide and have studied its coagulation for the first time.

The coagulation of negatively charged uranium ferrocyanide sol by different electrolytes has been determined at various dilutions of the sol. The most simple method for the preparation of colloidal ferrocyanide is to pour a dilute solution of an uranium salt into a solution of potassium ferrocyanide. Colloidal uranium ferrocyanide for these experiments has been prepared by pouring a dilute solution of uranium nitrate into a dilute solution of potassium ferrocyanide. The hydrosol thus formed is clear and has a deep red colour peculiar to uranium ferrocyanide. With increasing concentration of the uranium nitrate solution the sol becomes more and more turbid and finally coagulates. Colloidal uranium ferrocyanide thus obtained is dialysed for about 12 days when the wash water does not show any test for the ferrocyanide ion. The dialysed sol contains appreciable amount of ferrocyanide which can be easily detected by coagulating the sol and testing for ferrocyanide ion. As this sol has not been studied before, we have made experiments to find out whether this sol follows the Schulze-Hardy law or not. Table XV gives the results:—

TABLE XV

Concentration of the sol = 2.15 grams of uranium ferrocyanide per litre
3 c.c. of the sol is made up to 10 c.c. on mixing with the electrolyte;
Time = 2 hours

Electrolyte	Concentration	Amount added in c.c.	Precipitating concentration
KCl	N	2.6	0.2600
K_2SO_4	N	2.9	0.2900
$K_4Fe(CN)_6$	2N	1.65	0.3300
$BaCl_2$	N/25	1.50	0.0060
$MgCl_2$	N/25	1.95	0.0078
$Al(NO_3)_3$	N/100	0.85	0.00085
$Th(NO_3)_4$	N/200	1.40	0.00070

An examination of Table XV gives the following order for the precipitation values, beginning with the highest one:
$K_4Fe(CN)_6 > K_2SO_4 > KCl > MgCl_2 > BaCl_2 > Al(NO_3)_3 > Th(NO_3)_4$.

From this order it appears that the Schulze-Hardy law is applicable to this sol. The results of Pappadà on the coagulation of prussian blue sol and colloidal copper ferrocyanide show that the Schulze-Hardy law is also applicable to these sols.

It has been already reported that prussian blue sol behaves abnormally on dilution when coagulated by potassium chloride. Similar results have been obtained by Sen and Mehrotra[1] with a sol of copper ferrocyanide.

In Table XVI the results are given on the influence of dilution of uranium Ferrocyanide sol towards its coagulation by various electrolytes:

TABLE XVI

Concentration of the sol = 2.15 grams of uranium ferrocyanide per litre
Sol A = 3 c.c. sol made up to 10 c.c.
Volume = 10 c.c.; Time = 2 hours

Electrolyte	Amount to coagulate in c.c.		
	Sol 2A	Sol A	Sol A/3
KCl N	2.60	2.60	2.50
$K_2Fe(CN)_6$ N	2.90	2.90	3.00
$K_4Fe(CN)_6$ 2N	1.40	1.65	1.85
$BaCl_2$ N/25	1.70	1.50	1.30
$Al(NO_3)_3$ N/100	1.80	0.85	0.35
$Th(NO_3)_4$ N/200	2.85	1.40	0.55

It will be seen from these results that the amount of KCl or K_2SO_4 required to coagulate a dilute or a concentrated sol is practically constant, whilst a definite abnormality is observed with potassium ferrocyanide, that is, more of this electrolyte is necessary to coagulate a dilute sol than a concentrated one.

[1] Z. anorg. Chem., **142**, 345 (1925).

It is well-known that colloidal ferrocyanides are stabilised by the preferential adsorption of the ferrocyanide ion. I have observed that a hydrosol of uranium ferrocyanide is only stable when there is an excess of potassium ferrocyanide. A small excess of uranium nitrate causes complete coagulation of the sol. Potassium ferrocyanide in large excess coagulates the sol, because as the concentration of this electrolyte is gradually increased the adsorption of this electrolyte is gradually increased the adsorption of ferrocyanide ion reaches a maximum and finally the influence of the oppositely charged potassium ion becomes prominent and coagulates the sol.

We have observed that on shaking a well washed precipitate of uranium ferrocyanide with a dilute solution of potassium ferrocyanide traces of alkali are set free, probably due to the preferential adsorption of ferrocyanide ions. Duclaux[1] has shown that a great deal of potassium ferrocyanide is also taken up when copper ferrocyanide is precipitated, and that is is practically impossible to free cupric ferrocyanide from adsorbed potassium ferrocyanide. Duclaux, however, believes that potassium ferrocyanide is chemically combined with cupric ferrocyanide. In a recent paper Frankfert and Wilkinson[2] have found that alkalinity is developed when cupric ferrocyanide is shaken with $K_4Fe(CN)_6$. Working with two grams of cupric ferrocyanide and $_2N$ $K_4Fe(CN)_6$ solution they observed a total alkalinity of 200 c.c. of 0.01N KOH. On the addition of more concentrated solution of $K_4Fe(CN)_6$ the amount of alkali gradually decreased and finally the mixture became slightly acid. The development of the alkalinity is certainly due to the preferential adsorption of $Fe(CN)'''_6$ ion by cupric ferrocyanide, leaving its counterpart K' ion free, so that an excess of negative ion OH' must be found for maintaining electric neutrality of the solution. If, however, the amount of potassium ferrocyanide added is gradually increased, the preferential adsorption of ferrocyanide ion reaches a maximum, and on the continued addition of $K_4Fe(CN)_6$ the potassium ions, which are also present, become effective in coagulating the negatively charged sol with the liberation of an acid. We have observed that appreciable amounts of UO_2'' ions are adsorbed by uranium ferrocyanide and an appreciable amount of acid is developed when either a sol of uranium ferrocyanide is coagulated with uranium nitrate or a pure sample of uranium ferrocyanide is shaken with a solution of uranium nitrate. All attempts to prepare a positively charged sol of uranium ferrocyanide by the preferential adsorption of uranium ions, however, failed.

Gum Dammar Sol

The sol of this resinous substance is prepared exactly in the same way as the mastic sol. The resinous mass is powdered and dissolved in alcohol and the colloidal solution is obtained by pouring this alcoholic solution in a large volume of water. As gum dammar sol has not been investigated before, we have studied the coagulation of this sol by various electrolytes to find out if the Schulze-Hardy law is applicable to this sol.

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[1] J. Chim. phys., 7, 405 (1909).

[2] J. Phys. Chem., 28, 651 (1924).

In Table XVII our results are reproduced:—

TABLE XVII

Concentration of the sol[1] = 0.87 grm. gum dammar per litre
2 c.c. of the sol made up to 10 c.c.
Volume = 10 c.c.; Time = 1 hour

Electrolyte	Concentration	Amount added in c.c.	Precipitating concentration
KCl	N/2	2.65	0.1325
KNO_3	N/2	2.40	0.1200
K_2SO_4	N/2	2.80	0.1400
NaCl	N/2	2.80	0.1400
CH_3COONa	2N	1.25	0.2500
NH_4Cl	N/2	1.30	0.0650
HCl	N/100	0.80	0.0008
HNO_3	N/100	0.80	0.0008
$BaCl_2$	N/10	1.30	0.0130
$SrCl_2$	N/10	1.30	0.0130
$Al(NO_3)_3$	N/2,000	1.80	0.00009

An examination of Table XVII gives the following order of precipitation values for different electrolytes beginning with the highest one:— $CH_2COONa > K_2SO_4$, NaCl > KCl > $KNO_3 > NH_4Cl > BaCl_2$, $SrCl_2 >$ HCl, $HNO_3 > Al(NO_3)_3$. This shows that the Schulze-Hardy law is followed only partially, the exception being the H· ions, which possess greater coagulating power than bivalent Ba·· or Sr·· ions. Similar results are obtained on the coagulation of mastic sol, H· ions possessing greater coagulating power than bivalent Ba·· or Ca·· ions.[2] We have shown in a previous paper that this peculiar behaviour of hydrogen ions is due to the hydrolysis of sols of resinous substances like mastic, (gum dammar, gamboge etc. We have observed that the negatively charged gum dammar sol takes up a positive charge if quantities of $Al(NO_3)_3$ greater than its precipitating concentration are added all at once to this sol.

TABLE XVIII

Concentration of gum dammar sol = 0.87 grm. per litre
Sol A = 4 c.c. of the sol made up to 10 c.c.
Volume = 10 c.c.; Time = 1 hour

Electrolyte		Amount to coagulate in c.c.		
		Sol A	Sol A/2	Sol A/4
CH_3COONa	2N	1.25	1.40	1.80
KCl	N/2	2.00	2.65	3.00
KNO_3	N/2	——	2.40	2.70
$BaCl_2$	N/10	1.10	1.30	1.40
$Al(NO_3)_3$	N/2,000	2.50	1.80	1.30

[1] The concentration of the sol has been estimated by evaporating a known volume of the sol on a water-bath in a platinum crucible.

[2] Compare Freundlich: "Kapillarchemie," 367 (1909).

In Table XVIII the results showing the influence of change of concentration of gum dammar sol towards its coagulation by various electrolytes are recorded.

These results are similar to those obtained by us with mastic sol when coagulated at various concentrations and this sol behaves abnormally on dilution when coagulated by both univalent and bivalent cations. It is interesting to observe here that when arsenious sulphide and antimony sulphide sols are coagulated with bivalent cations like $Ba^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, etc., the amounts of these cations required to coagulate a dilute or a concentrated sol are practically constant. Our results in Table XVIII are unlike those obtained with arsenious and antimony sulphide sols and show that the sols of gum dammar and of mastic are not only abnormal on dilution towards monovalent electrolytes like KCl, KNO_3, etc., but are also abnormal towards bivalent electrolytes like $BaCl_2$, $SrCl_2$, etc. The abnormality on dilution is more marked when the sol of gum dammar is coagulated by KCl or KNO_3 than that observed when it is coagulated by $BaCl_2$. Greater amounts of $Al(NO_3)_3$ are, however, required to coagulate a concentrated sol than a dilute one and the general dilution rule is applicable to the coagulation of this sol by aluminium nitrate.

Gamboge Sol

This sol has been studied because it closely resembles the sols of mastic and gum dammar in its chemical properties. The sol has been prepared by the same method as that adopted in the preparation of the sols of mastic and gum dammar.

In Table XIX the results are given as obtained by us when gamboge sol is coagulated at different dilutions by various electrolytes:—

TABLE XIX

Concentration of the sol = 0.388 grm. gamboge per litre
Sol A = 5 c.c. of the sol made up to 10 c.c.
Volume = 10 c.c.; Time = 1 hour

Electrolyte		Amount to coagulate in c.c.		
		Sol A	Sol A/2	Sol A/4
KCl	2N	0.90	1.80	2.40
$BaCl_2$	N/5	0.90	0.90	0.95
$Al(NO_3)_3$	N/2,000	0.95	0.50	0.45

These results prove that gamboge sol behaves abnormally on dilution when coagulated by either KCl or $BaCl_2$, whilst it behaves normally on dilution when coagulated by aluminium nitrate. Gamboge sol, therefore, behaves exactly like mastic and gum dammar sols on dilution when coagulated by various electrolytes.

Sulphur Sol (Weimarn)

Odén[1] has studied the coagulation of colloidal sulphur prepared by the action of an acid on a sodium thiosulphate solution. His results show that the Schulze-Hardy law fails in this case, a few univalent ions possess greater coagulating powers than many bivalent ions. Odén has also investigated the influence of dilution on the stability of this sol towards many electrolytes and his data show that whilst the sol behaves as a more stable one and requires greater quantities of an univalent coagulating ion to precipitate a dilute sol than a concentrated one, the amount of bivalent and trivalent ions required to coagulate the sol decreases with the decreasing concentration of the sol. Colloidal sulphur prepared by Weimarn's method shows less deviations from the Schulze-Hardy law,[2] and as the influence of concentration of this sol towards its coagulation has not been studied, we have taken up this problem.

The sol was prepared by dissolving γ-sulphur in alcohol and pouring the alcoholic solution into a large volume of water. The sol is extremely unstable and coagulation begins in the sol when kept for more than a week.

The experimental results, given in Table XX, were obtained with a Weimarn sulphur sol and the coagulation experiments were carried on the same day as the sol was prepared.

TABLE XX

Sol A = 4 c.c. of the original sol made up to 8 c.c.
Volume = 8 c.c.; Time = ½ hour

Concentration of the sol.	KCl N/2 added in c.c.	BaCl$_2$ N/25 added in c.c.
A	1.0	1.05
A/2	0.85	0.5
A/4	0.79	0.2

From the above results it is obvious that less of monovalent and bivalent electrolytes are necessary to coagulate the dilute sol than a concentrated one. The data are not very accurate as it is very difficult to obtain exactly reproducible results.

Gold Sol

Coagulation of this sol has been investigated by several workers[3] in this field. Recently Freundlich and Scholz[4] have studied the coagulation of the sol with a mixture of electrolytes of widely varying valencies. Their sol was prepared according to the method of Donau[5] by reducing $HAuCl_4$ to metallic gold by carbon monoxide. The influence of change of concentration of gold sol on its coagulation has not been studied before, and it was, therefore, considered desirable to investigate this problem.

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[1] "Der kolloide Schwefel," 156 (1912).
[2] Compare Freundlich: "Kapillarchemie," 849 (1922).
[3] Compare Freundlich: "Kapillarchemie," 576 (1923).
[4] Kolloidchem. Beihefte, **16**, 267 (1922).
[5] Monatsheft, **26**, 525 (1905).

The sol was prepared according to the method of Zsigmondy[1] by reducing a solution of $HAuCl_4$ with formaldehyde in presence of small quantities of K_2CO_3. In Table XXI the results are recorded as obtained when gold sol is coagulated at different concentrations by various electrolytes:

TABLE XXI

Concentration of the sol = 0.065 grm. gold per litre
Sol A = 4 c.c. of the sol made up to 6 c.c.
Volume = 6 c.c.; Time = 1 hour

Electrolyte		Amount to coagulate in c.c.		
		Sol A	Sol 3A/4	Sol A/2
KCl	N/5	2.00	1.80	1.65
KNO_3	N/5	2.10	1.90	1.80
KOH	N/2	2.00	1.90	2.00
$K_2C_2O_4$	N/2	1.65	1.70	1.70
$BaCl_2$	N/50	1.00	0.90	0.75
$Al(NO_3)_3$	N/1,000	0.80	0.55	0.35

Table XXI shows that greater amounts of KCl, KNO_3, $BaCl_2$ and $Al(NO_3)_3$ are required to coagulate a concentrated gold sol than a dilute one, and, therefore, obeys the general dilution rule. On the other hand, when gold sol is coagulated with either KOH or $K_2C_2O_4$ the quantities of these electrolytes required to coagulate a dilute or a concentrated sol are practically constant and have a tendency to behave abnormally towards dilution when coagulated by KOH and $K_2C_2O_4$. These results are very interesting and prove that the abnormality of gold sol on dilution towards its coagulation by KOH and $K_2C_2O_4$ is certainly due to the adsorption of anions from these electrolytes and its consequent stabilisation by this adsorption of ions carrying the same charge as the sol.

In Table XXII the precipitation values of various potassium compounds determined for Sol A are given:—

TABLE XXII

Electrolyte	Concentration	Amount added in c.c.	Precipitation value
KCl	N/5	2.00	0.0667
KNO_3	N/5	2.10	0.0700
KOH	N/2	2.00	0.1667
$K_2C_2O_4$	N/2	1.65	0.1375

The precipitation values of the potassium compounds investigated are in the order KOH > $K_2C_2O_4$ > KNO_3 > KCl, beginning with the electrolyte possessing the highest precipitation value. The great difference in the precipitation values of either $K_2C_2O_4$ or KOH from those of KCl or KNO_3 is obviously due to the greater amount of adsorption of OH' or C_2O_4'' ions than that of Cl' or NO'_3. This conclusion has been further substantiated by our researches on the coagulation of this sol with a mixture of electrolytes and on the phenomenon of acclimatization.

[1] Z. anal. Chem., 40, 711 (1901).

In a recent paper Morris and Harris[1] have also emphasised the marked influence of anions on the coagulation of gold sol and from their experiments on the coagulating power of several sodium salts, they have obtained the following order showing the influence of anions on its coagulation:—C_2O_4'' > HPO_4'' > CO_3'' > OH', citrate$'''$ > HCO_3' > Br' > I', acetate$'$ > valerate$'$ > butyrate$'$, CNS' > SO_4'' > Cl' > benzoate$'$.

The above order proves conclusively that C_2O_4'' and OH' ions possess far greater stabilising influence on the coagulation of gold sol than that of Cl' ions. These results of Morris and Harris are, therefore, in line with the results obtained by us on the coagulation of gold sol.

Silver Sol

The sol was prepared according to the method of Kohlschütter[2] by reducing a solution of Ag_2O in a current of hydrogen at 60°. The sol thus obtained, however, contains enough of OH' ions as an impurity and it is practically impossible to reduce Ag_2O completely by this method.

The experimental results on the coagulation of this sol at different concentrations by various electrolytes are given in Table XXIII.

TABLE XXIII

Concentration of the sol = 0.18 grm. Ag per litre
Sol A = 4 c.c. of the original sol made up to 6 c.c.
Volume = 6 c.c.; Time = 1 hour

Electrolyte		Amount to coagulate in c.c.		
		Sol A	Sol 3A/4	Sol A/2
NaOH	N/5	1.20	2.05	2.80
KNO_3	N/8	1.90	2.10	2.10
$Ba(NO_3)_2$	N/625	1.80	1.75	1.75
$Al(NO_3)_3$	N/5,000	1.40	1.30	0.95

The foregoing results show that the sol behaves abnormally towards dilution when it is coagulated with either KNO_3 or NaOH, but the abnormality is far more developed with NaOH than with KNO_3. This is certainly due to the fact that OH' ions possess a great stablising influence on this sol. On the other hand, practically constant amounts of $Ba(NO_3)_2$ are required to coagulate a concentrated or a dilute sol, and with $Al(NO_3)_3$ the general dilution rule that the greater the concentration of the sol the greater is the amount of an electrolyte necessary for coagulation is obeyed.

It will be interesting to point out here that the silver sol obtained by Kohlschütter's method is by no means pure. In a very recent paper Erlach and Pauli[3] have shown that this sol even on dialysis contains varying quantities of silver hydroxide, some times as much as twenty per cent. The considerable amount of OH' ions available from silver hydroxide possess a great

[1] Trans. Faraday Soc., **25**, 30 (1924).
[2] Z. Elektrochem., **14**, 49 (1908).
[3] Kolloid-Z., **34**, 213 (1924).

stabilising influence and it is, therefore, difficult to draw any definite conclusion about the adsorption of NO'_3 ion from either KNO_3 or $Ba(NO_3)_2$. The influence of OH' ions will be discussed in a subsequent paper.

Summary and Conclusion

From the experimental results advanced in the foregoing pages, it will be seen that the following sols follow the general dilution rule, viz., the greater the concentration of the sol the greater is the amount of an electrolyte necessary for coagulation: (1) stannic hydroxide (positive); (2) manganese dioxide (negative); (3) manganese dioxide (positive); (4) aluminium hydroxide; (5) vanadium pentoxide; (6) thorium hydroxide; (7) sulphur (Weimarn); and (8) gold.

The following sols do not follow the general dilution rule and hence behave abnormally, when coagulated by univalent and sometimes by bivalent ions: (1) antimony sulphide; (2) prussian blue; (3) gum dammar; and (4) gamboge.

Uranium ferrocyanide sol is practically on the border line. A sol of metallic silver is abnormal towards dilution when coagulated by univalent electrolytes because it is usually associated with silver hydroxide of which OH' ions are highly adsorbed by a sol of silver.

We have proved in the foregoing pages that when positively charged manganese dioxide sol is coagulated by $AgNO_3$ or $CuCl_2$, the sol requires more of these electrolyte to coagulate it in the diluted condition than that required to coagulate the concentrated one. This abnormal behaviour is certainly associated with the marked adsorption of Ag or Cu ions by manganese dioxide.

From the foregoing results it will be clear that those sols, which do not adsorb an ion carrying the same charge as the sol, follow the general dilution rule, whilst those sols, which are capable of adsorbing an ion carrying the same charge as the sol are normal. Hence from our experimental researches it will be clear that the adsorption of an ion carrying the same charge as the sol plays a very important part in the coagulation of sols.

In previous papers published from this laboratory it has been proved that sols like arsenious sulphide, antimony sulphide, mastic, gamboge, gum dammar, prussian blue, copper ferroyanide etc. are appreciably hydrolysed in presence of water and this hydrolysis makes these sols stable towards electrolytes. It is well known that the degree of hydrolysis of a substance increases with dilution; consequently, these sols become more stable towards electrolytes because of increased hydrolysis. We have also shown that hydrogen ions check the hydrolysis of these sols, which behave abnormally when coagulated by KCl, LiCl, etc., but all these sols have a tending to behave normally when coagulated by acids, which check the hydrolysis of the sols considerably and make them unstable towards electrolytes.

Chemical Laboratory
University of Allahabad
Allahabad, India.

DYNAMIC SURFACE TENSION AND THE STRUCTURE OF SURFACES

BY OSCAR KNEFLER RICE

Sudden extension or contraction of a surface may affect the instantaneous value of the surface tension in two ways. In the first place it may do so by causing a change in the temperature at the surface, Gibbs[1] having shown that this will always result in an increase in tension on expansion and a decrease on contraction. If there are two or more components the surface tension may be affected because of the slowness of establishment of equilibrium due to the slowness with which substances in the solution diffuse to the surface. The latter effect should be the more important one, as thermal equilibrium is undoubtedly established much more quickly. This case has also been discussed by Gibbs[2], as follows. Since the substances which diminish surface tension tend to be adsorbed at the surface, sudden expansion of the surface will leave the solution near the surface poorer in these substances. There will therefore be an increase of surface tension if we can assume that the general character of the results is to be given by supposing that equilibrium is established at the surface and some little way back, but not throughout the solution. Contraction, on the other hand, by creating an excess of the substances which diminish surface tension in the neighborhood of the surface, will cause a decrease of surface tension.

But we may still inquire as to just what would happen if the surface were so rapidly extended that partial equilibrium were very far from being established. We may gain some information on this subject by looking at the matter from a molecular kinetic point of view. The molecules which tend to crowd to the surface are the ones on which the intermolecular attractive forces are the least. But the surface tension, according to Laplace and van der Waals, depends on the molecular forces at the surface, and these will be least when as many as possible of the weakly attracted molecules have had time to get to the surface. Very rapid contraction, on the same basis, will cause a decrease of the surface tension, as there will be too many of the weakly attracted molecules near the surface. This, however, is not very rigorous, and does not help us if, for example, we wish to consider the case of a pure liquid in which the molecules are normally oriented, but whose surface is extended so rapidly as to allow no time for orientation[3]. It is true, of course, that orientation would probably take place even faster than thermal equilibrium would be established, so the effect would be masked and unobservable, but we can at least consider it in theory.

[1] Gibbs: "Scientific Papers," **1**, 269 (1906).

[2] Gibbs: *loc. cit.*, p. 272.

[3] Such an effect must not be confused with that due to the presence of several different *species of molecules, arising from association, in a pure liquid. See Lenard: Sitzungber.* Heidelberger Akad., **1910**, 18; see also Bancroft: "Applied Colloid Chemistry," p. 134 (1921), on the effect of a surface transition layer.

We may avoid all difficulties by a single thermodynamic proof, which covers every situation, apart from the thermal effects, and which, in spite of its simplicity, is not, to my knowledge, to be found in the literature.

Relation between Dynamic and Static Surface Tensions

Suppose that we start with a body of liquid and very rapidly increase its surface by unity, so that no time is allowed for equilibrium to be established at the surface. The process under these conditions is nevertheless reversible, and the free energy change is therefore given by γ', the instantaneous value of the surface tension, or, as we shall call it, the dynamic surface tension of extension. Now let the surface come to equilibrium with a change of free energy, a, which must be negative. Now change the surface back to its original size reversibly and slowly, the change in free energy being γ the ordinary, or static, surface tension. The system is then back to its original condition, and the change of free energy in the cycle must have been zero, or

$$\gamma' - \gamma + a = 0 \qquad (1)$$

Hence

$$\gamma' > \gamma \qquad (1a)$$

as a is negative.

Now in a similar manner, by first increasing the surface slowly, then decreasing it rapidly, and then allowing equilibrium to be established by diffusion, we show that the dynamic surface tension of contraction is less than the static surface tension.

In what follows we shall not have any occasion to deal with the dynamic surface tension of contraction, and we shall refer to that of extension simply as the dynamic surface tension.

In some cases the dynamic surface tension may be measured by a method which does not actually bring about an extension of the surface, but which by providing fresh surface affects the composition in the neighborhood of the surface in the way extension would affect it. The surface tension resulting from such a process is the same as the dynamic surface tension of extension (aside from thermal effects).

Review of the Literature

Any experimental data that one can bring to bear on the subject is unsatisfactory. There have been numerous determinations of surface tensions by various methods, many of them giving contradictory results; besides there is always the difficulty in deciding whether a method will give dynamic or static surface tension. In no case, I believe, has a method been used which would give dynamic surface tension of contraction. The following account is to be considered merely as illustrative of what may be found in the literature.

One means of getting a fresh surface is the use of an oscillating jet. This was first used by Rayleigh, and a summary of his results is given by Freundlich[1] and by Bancroft[2], together with measurements of the same solutions by a

[1] Freundlich: "Kapillarchemie," 735 (1922).
[2] Bancroft: *loc. cit.*, p. 132.

static method. Using sodium oleate and saponine solutions, he found in every case that the dynamic surface tension was considerably greater than the static. He detected no difference between the dynamic and static surface tensions of water.

Bohr[1] measured the surface tension of water by this method, getting 72.35 dynes per cm. (corrected to 18°C.) against the static value of about 72.9. Stocker[2], using this method, got a value of 72.51 for water at 18°C. He also measured some surface tensions of salt solutions, the results usually being about a half dyne low, but in some cases being about a dyne below the static values. These results are contrary to our expectation[3]. Lenard[4] has stated his belief that the dynamic value should be higher, and he notes that when Bohr and others measure nearer the orifice their values exceed that of the ordinary static surface tension, which he explains as being due to the fact that the surface near the orifice is fresher, but which Bohr would say was due to hydrodynamical disturbances.

We may also mention the experiments done by Pedersen[5] by this method. He finds for water at 15°C. the value 74.30, which is high. He finds for toluene at 15° the value 28.76, agreeing with Volkmann's result of 28.79 by the capillary rise method, but for aniline he gets 43.00 as contrasted with Volkmann's 44.30, and Feustal's 46.6 (which was done by the method of maximum pressure in small bubbles).

It is well known that fresh mercury surfaces in the presence of gases have a higher surface tension than old ones.[6]

Grünmach[7] using a capillary ripple method, which does not however seem to be a very satisfactory way, finds that alcohol in which the surface is being continually renewed has a surface tension nearly seven dynes lower with an old surface, and similar, but not such marked differences with water.

Hiss[8] used a capillary rise method for determining surface tension. In every case but one Hiss found the dynamic to be higher than the static surface tension, and in this one case he concluded that the two were equal, but it must be noted that if the dynamic were lower he would not have found it by his method.

Case where Equilibrium is established for the Solvent but not for the Solute

Hiss's experiments are valuable in that they give an idea of the actual variation of the surface tension with the time. His experiments on soap solutions showed that the time required for the final value of the tension to be reached was considerably greater than was the case for pure water. It may

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[1] Bohr: Phil. Trans., **209** A, 281 (1909).
[2] Z. physik. Chem., **94**, 149 (1920).
[3] No significance can be attached to the comparison of measurements on ammonia solutions given by Stocker, due to the high vapor pressure of ammonia from these solutions.
[4] Lenard: loc. cit.
[5] Pedersen: Phil. Trans., **207** A, 381 (1908).
[6] See Bancroft: *loc. cit.*, p. 133.
[7] See Pedersen: loc. cit., pp. 387, 381.
[8] Hiss: Diss. Heidelberg (1913).

thus be possible to study dynamic surface tensions when the surface is of such an age that for pure water at that age the surface tension would have its static value. In this case the difference in the dynamic and static surface tension would be attributed to the solute alone. This was likely the case, at least in part, in Rayleigh's experiments, and in some done by du Noüy[1] with very dilute sodium oleate solutions for which he found it required some hours to get the static surface tension.

In view of this it may be of some interest to develop a theory for the dynamic surface tension when it is assumed that equilibrium is established as far as solvent is concerned, but not established at all with respect to solute.

Now we can see offhand that the more the adsorption is confined to a narrow region of the liquid near the surface the greater the difference in the dynamic and static surface tensions will be; for the higher the concentration (or the lower, if the adsorption is negative) of the solute in that region will be for a given amount of material adsorbed, and therefore the greater the change in concentration and hence in free energy when equilibrium is established after a rapid increase of surface. (The concentration of the solvent does not concern us, as equilibrium is attained for it.) We will develop this idea from a more mathematical point of view later, and get some idea as to the magnitude of the effect.

We may also note that the more adsorption is confined to a narrow region the more slowly we should expect equilibrium to be established. There are, therefore, two reasons for the difference in dynamic and static surface tension to be particularly noticeable if the adsorption is so confined, one being a thermodynamic one and the other depending on a rate of diffusion.

We will now proceed to the mathematical development, under the assumption that there is no change in volume in any of our processes. Our method of attack will consist in an evaluation of the quantity a in equation (1).

We will let n be the concentration of the dissolved material in the solution far from the surface, and n_x its concentration at a distance x from the surface. If u is the amount of adsorption per unit surface, then $u = \int_0^\infty (n_x - n)dx$.

We will consider a cycle of operations which take place at a certain definite concentration, and we will carry on our processes in such a way that $n_x - n/u$ is a function of x and n only, not a function of u. That is, while the amount of substance adsorbed may vary, its distribution never is allowed to, for it will be seen that $(n_x - n)/u$ indicates the relative amount of adsorption at the point x.

Let $\bar{F}$ be the partial free energy of the solute in the solution, $\bar{F}_x$ the partial free energy at a distance x from the surface (i.e., the free energy of transfer of unit amount of solute from the corresponding point in a solution whose n_x is unity to the proper point in the given solution), and $\triangle F_x$ the free energy of transfer from an infinite distance in the solution to the point in question when both n and n_x are equal to unity. Let γ and γ' have the previously assigned meanings.

[1] Du Noüy: Compt. rend., **178**, 1102 (1924).

As stated, our proposition is now to evaluate a in terms of these quantities. In the case we are considering a is the free energy change which takes place when equilibrium is established after the surface has been very rapidly extended, or the free energy of transfer of a certain amount of material from the interior of the solution to its proper place at the surface (or from the surface to the interior, in which case we give it a negative value). We assume the system to be so extensive that the concentration in the interior of the solution is not appreciably affected by such a transfer.

Now if we bring a certain amount of the solute, du, to unit area of the surface, the part which lies between x and $x+dx$ receives an amountd $(n_x-n)\,dx$. As we are going to effect this transfer in such a manner that $(n_x-n)/u$ is a constant and equal to $(n_{x1}-n)/u_1$, where n_{x1} and u_1 are the values which are finally going to be assumed when equilibrium is reached, we have

$$n_x - n = \frac{n_{x1}-n}{u_1}\,u \text{ or } d(n_x-n) = \frac{n_{x1}-n}{u_1}\,du$$

In order to effect this transfer there was a change of free energy equal to $(-\bar{F}+\triangle F_x+\bar{F}_x)\frac{n_{x1}-n}{u_1}\,dx\,du$ and integrating over the entire surface layer, and over the entire period of adsorption in which u varies from o to u_1, we get

$$a = \int_o^{u_1}\int_o^{\infty}(-\bar{F}+\triangle F_x+\bar{F}_x)\left(\frac{n_{x1}-n}{u_1}\right)dxdu \qquad (2)$$

Now if we remember that $\bar{F}$ is independent of both u and x and that $\int_o^{\infty}(n_{x1}-n)dx = u_1$, we may perform part of the integration indicated in (2), getting

$$a = \int_o^{u_1}\int_o^{\infty}(\triangle F_x+\bar{F}_x)\left(\frac{n_{x1}-n}{u_1}\right)dxdu + \bar{F}u_1 \qquad (3)$$

Now if we put (3) in equation (1) this will give us the equation we have been striving to obtain.

We may get more information however if we first differentiate (1) with respect to n as independent variable under the condition that equilibrium be everywhere maintained between the surface and the interior of the solution. This gives us

$$\frac{d\gamma'}{dn} = \frac{d\gamma}{dn} - \left(\frac{\partial a}{\partial n}\right)_{u_1} - \left(\frac{\partial a}{\partial u_1}\right)_n \frac{du_1}{dn} \qquad (4)$$

Now we will use (2) in the evaluation of $(\partial a/\partial u_1)_n$ and (3) in the evaluation of $(\partial a/\partial n)_{u_1}$. In doing this we must remember that $\left[\frac{\partial}{\partial n}\left(\frac{n_{x1}-n}{u_1}\right)\right]_{x,u_1}$ will not in general be zero, but $\left[\frac{\partial}{\partial u_1}\left(\frac{n_{x1}-n}{u_1}\right)\right]_{x,n}$ will. When we differentiate

partially with respect to u_1 we do so holding the distribution of solute at the surface constant, and it amounts to differentiation with respect to the upper limit. The partial differentiation with respect to n is to take into account the effect of any change in distribution at the surface. Thus (4) becomes

$$\frac{d\gamma'}{dn} = \frac{d\gamma}{dn} - \frac{\partial}{\partial n}\left[\int_o^{u_1}\int_o^{\infty}(F_x + \triangle F_x)\left(\frac{n_{x1} - n}{u_1}\right)dxdu\right]_{u_1} - \frac{\partial \bar{F}}{\partial n}u_1$$
$$- \frac{du_1}{dn}\left[\int_o^{\infty}(-\bar{F} + \triangle F_x + \bar{F}_x)\left(\frac{n_{x1} - n}{u_1}\right)dx\right] \qquad (5)$$
$$u = u_1$$

By the condition of equilibrium $-\bar{F} + \triangle F_x + \bar{F}_x$ vanishes when u is equal to u_1, so the coefficient of du_1/dn vanishes; also we know by Gibbs's adsorption equation that $\frac{d\gamma}{dn} = -u_1\frac{\partial \bar{F}}{\partial n}$ Using this relation, and putting the differentiation under the integral sign, we have

$$\frac{d\gamma'}{dn} = -\int_o^{u_1}\int_o^{\infty}\frac{\partial}{\partial n}\left\{(F_x + \triangle F_x)\left(\frac{n_{x1} - n}{u_1}\right)\right\}dxdu \qquad (6)$$

We may now investigate the form this takes if we may assume solutions to be perfect. In this case $n_{x1} = ne^{-\frac{\triangle F x}{RT}}$ and as $u_1 = n\int_o^{\infty}(e^{-\frac{\triangle F_x}{RT}} - 1)\,dx$ it is seen that $(n_{x1} - n)/u_1$ is independent of n. Also $\left(\frac{\partial \bar{F}_x}{\partial n}\right) = \frac{\partial \bar{F}_x}{\partial n_x}\left(\frac{\partial n_x}{\partial n}\right)$ while $\frac{\partial \bar{F}_x}{\partial n_x} = \frac{RT}{n_x}$ where R is the gas constant and T the temperature and $\left(\frac{dn_x}{n\partial}\right) = 1$ because $\frac{n_x - n}{u} = \frac{n_{x1} - n}{u_1}$ is a constant. Also it is always true that $(\partial\triangle F_x/\partial n)$ is zero, for $\triangle F_x$ depends only on x. So

$$\frac{d\gamma'}{dn} = -\int_o^{u_1}\int_o^{\infty}\frac{RT}{n_x}\frac{n_{x1} - n}{u_1}dxdu$$
$$= -\int_o^{\infty}\int_o^{u_1}\frac{RT}{n_x}\frac{n_{x1} - n}{u_1}dudx$$

$\frac{n_{x1} - n}{u_1}$ and n are independent of u in the integration, so expressing n_x in terms of $\frac{n_{x1} - n}{u_1}$, n and u, by means of the equation $\frac{n_x - n}{u} = \frac{n_{x1} - n}{u_1}$ and performing the integration with respect to u, we get

$$\frac{d\gamma'}{dn} = -RT\int_o^{\infty}\log\frac{n_{x1}}{n}dx\left(= -\int_o^{\infty}\triangle F_x\,dx\right) \qquad (7)$$

As in the case of perfect solutions $\frac{d\gamma}{dn} = -\frac{RTu_1}{n} = -\frac{RT\int_o^\infty (n_{x1} - n)\,dx}{n}$,

we have for purposes of comparison,

$$\frac{d\gamma'/dn}{d\gamma/dn} = \frac{\int_o^\infty \log n_{x1}/n\ dx}{\int_o^\infty (n_{x1}/n - 1)\,dx}$$

Now let us call $n_{x1}/n - 1$, which is a quantity which expresses the proportion of the adsorption which takes place at a particular place x, z. We may then write

$$\frac{d\gamma'/dn}{d\gamma/dn} = \frac{\int_o^\infty \log (z+1)\,dx}{\int_o^\infty z dx} \qquad (8)$$

Now if the adsorption is positive z is always greater than zero and $\log (z+1)$ is always less than z. The larger z is the smaller the ratio $\frac{\log (z+1)}{Z}$ and the smaller z the nearer the ratio is to 1. Now suppose the chief contribution to u_1 is in some very narrow region so that z is very large in this region, then, of course $d\gamma'/dn$ is absolutely very much smaller than $d\gamma/dn$ (which means, as they are both negative, that γ' is larger than γ). In other words the more the adsorption is confined to a narrow region, i.e., the nearer the adsorbed substance comes to forming a monomolecular layer, the less the dynamic surface tension of the solution should differ from that of the pure solvent. Let us make a calculation assuming z to be constant over a distance of molecular dimensions, say 10^{-8} cm., and zero elsewhere, assuming that $d\gamma/dn = -10$ dynes per mole per liter, and that T is 300° absolute. This makes $\int_o^\infty z dx = \frac{d\gamma}{dn} \Big/ RT = 4 \times 10^{-7}$ in C. G. S. units (changing liters to cc.) Since $\int_o^\infty z dx = z \times 10^{-8}$ by the assumptions we have made we find that z is about 40 and $\frac{d\gamma'}{dn} = \frac{d\gamma}{dn}\frac{\log 40}{40} = .08\,\frac{d\gamma}{dn}$.

If the adsorption is negative and z is always less than zero, $\log (z+1)$ is always greater than z, absolutely. It will be seen that z does not become less than -1, and if z is -1, $\log (z+1)$ is infinite. In this case the change of surface tension with the concentration of the solute is positive, so if the region of adsorption is narrow it means a high value of the dynamic surface tension for a given amount of adsorption, and there is no theoretical limit to the value it might reach.

The Surface Tension of Sodium Oleate Solutions

Recently du Noüy[1] has determined the surface tension of very dilute sodium oleate solutions, using a ring tensimeter. He found that the surface tension of very dilute solutions was very close to that of water, except in the neighborhood of three very sharply defined minima. He also showed, by an apparently unassailable argument, that practically all the sodium oleate was

[1] Du Noüy: *Phil. Mag.*, (6) **48**, 664 (1924).

on the surface of the solution and that these three minima corresponded to points where the molecules completely covered the surface in a monomolecular layer, each minimum corresponding to a definite orientation of the molecules of the surface. Du Noüy considers that his method gives a static surface tension. He found, as in his earlier experiments, that the initial value of the surface tension for these dilute solutions was always about that of water, and that it was only after long standing that the final value was reached.

If we attempt to calculate the dynamic surface tension of such solutions we meet with the obvious difficulty that the perfect solution laws cannot hold clear up to the surface. But we would surely expect that it would be somewhat near that of water. One thing is certainly true, $d\gamma/dn$ is very much greater in absolute magnitude than the 10 dynes per cm. per mole used in the example, and this factor would have the effect of making z very much larger and hence $\frac{d\gamma'}{dn} \Big/ \frac{d\gamma}{dn}$ smaller than the values we have calculated.

Rayleigh, in the experiments we have already mentioned, also found the dynamic surface tension of sodium oleate solutions to be nearer the surface tension of water than the static. In some cases Rayleigh actually found a greater value for the dynamic surface tensions of these solutions than that of the static surface tension of water. Whether this is a spurious effect, or whether it could be explained if all the factors could be taken into account, is something we cannot at present judge.

We may perhaps be pardoned if we insert at this point a slight digression concerning the interpretation of du Noüy's results. We will grant, what seems extremely probable, that practically (but, of course, not quite) all of the sodium oleate is at the surface of the solution. However this may be, *very* dilute solutions must be perfect even at the surface, and we have Gibbs's equation holding in the form[1] $\gamma_0 - \gamma = RTu_1$ (where γ_0 is the surface tension of pure water. This will not hold for any appreciable concentration, but we can always write Gibbs's equation in the form $d\gamma = -RTu_1 \, d\log n$ as the perfect solution laws will surely hold far from the surface, it only being near the surface that the concentration is high. n, it must be remembered is the concentration in the interior of the solution, and has no direct connection with the amount which has been added. To better see what happens as sodium oleate is added, we may write $\log n = f(u_1)$ or $d \log n = f'(u_1)du_1$, u_1 being a convenient quantity to take as independent variable because it is approximately proportional to the amount that has been added. In order to account for the large regions in du Noüy's curve in which the surface tension does not vary we must suppose that n or $f(u_1)$ remains nearly constant (and it will be very small) over wide ranges of the value of u_1. We must also suppose that as u_1 is continually increased that n finally increases, reaching a maximum when the surface tension is a minimum (if we neglect the effect of the variation of u_1 itself in Gibbs's equation), then, as u_1 becomes still larger,

[1] See Herzfeld: Z. physik. Chem., **107**, 79 (1923).

actually *decreases*, and that this occurs at each minimum of du Noüy's curve. The maximum value of n would correspond to a completely covered surface with all the molecules in a definite state of orientation. Then, as we crowd more molecules into the surface by changing their orientation we must suppose that their escaping tendency from the surface grows less.

In order to escape this inherently improbable situation, the only alternative that I can see is to suppose that the ring tensimeter, depending as it does on the force necessary to rupture a film, does not give the static surface tension as we have implicitly assumed, but that the "degree of staticness," if we may be allowed the use of such an expression, is determined by the state of the film at the surface, being greatest when the surface is as completely as possible filled with molecules in a certain definite state of orientation, a practically entirely dynamic surface tension being obtained except in the immediate neighborhood of such points.

Summary

The theory of dynamic surface tension is developed from a new point of view, a proof being given on simple thermodynamic grounds that thedynamic surface tension when the surface is extended is greater than the static and when the surface is contracted is less. The above is discussed in connection with other possible points of view. A recapitulation of some of the data in the literature bearing on the subject is given.

It is possible that equilibrium might be established between all parts of the solvent, but not established between the portions of the solute which are respectively near the surface and far from it. A discussion of this possibility is given, considering only the dynamic surface tension of extension, and it is shown that the narrower the region to which adsorption is confined (in the normal situation after equilibrium is established) the larger will be the value of the dynamic surface tension. If perfect solution laws hold clear to the surface the dynamic surface tension can never be greater than the (static) surface tension of the pure solvent if the adsorption is positive, but in case the adsorption is negative an infinite value of the dynamic surface tension is theoretically possible.

Du Noüy's determination of the surface tension of sodium oleate solutions is discussed and his results explained (in apparently the only possible way) on the assumption that his method of the ring tensimeter does not give true static values of the surface tension, but that the "degree of staticness" is determined by the state of the molecules at the surface.

Department of Chemistry,
The University of California,
Berkeley, California.

-H 216

THE GASEOUS REACTION BETWEEN HYDROGEN SULPHIDE AND SULPHUR DIOXIDE

BY H. AUSTIN TAYLOR AND W. ANDREW WESLEY[1]

The most important problem which confronts the physical chemist today is the determination of the mechanism of chemical reaction. The interaction of solids is relatively unimportant and the behavior of substances in solution seems in most cases to be highly complex. Therefore great interest attaches to the study of gaseous reactions and the elucidation of their mechanisms.

The rapidity with which hydrogen sulphide and sulphur dioxide react in aqueous solution and the fact that even the most reactive substances become inert upon complete desiccation[2] suggested that reaction may proceed at a much slower rate, if at all, between the dry gases. Although it has been known for at least a century that hydrogen sulphide does react with sulphur dioxide according to the equation:

$$2H_2S + SO_2 = 3S + 2H_2O$$

nothing definite was known of the manner in which these gases combine in the absence of a liquid phase except that the end products are sulphur and water. The work herein discussed is a study of the kinetics of the reaction, data of which are most valuable in deciding the mechanism of the reaction. The results indicate clearly that the gases are brought into an active condition by adsorption on the walls of the reaction tube, and combine to a very small extent, if at all, in the gaseous phase.

The demonstration of the rapid reaction between hydrogen sulphide and sulphur dioxide in the presence of excess moisture was a common lecture experiment as early as 1812, but it is not known by whom this reaction was first observed. However, Cluzel[3] noted at that time that no combination would result if the gases were first dried by passing over calcium chloride. Many investigators[4] have studied the reaction in a more or less qualitative way, but their results throw little light on the gaseous reaction because they permitted water to condense in the reaction system.

The equilibrium in the reaction has been recently studied in California. Lewis and Randall[5] were unable to use the method of determining equilibrium by rapidly cooling the reacting substances and analyzing, because the reaction occurs "rapidly in either direction according to the conditions imposed."

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[1] Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University.

[2] Baker: J. Chem. Soc., **65**, 623 (1894); Mellor and Russel: **81**, 1272 (1902).

[3] Ann. Chim. Phys., **84**, 162 (1812).

[4] Mulder: Jahresb., **1856**, 86; Corenwinder: Compt. rend., **53**, 140 (1861); Gripon: **56**, 137 (1863); Meyers: J. prakt. Chem., **108**, 123 (1869); Compt. rend., **74**, 195 (1872).

[5] J. Am. Chem. Soc., **40**, 362 (1918).

They were obliged to use a static manometric method with an excess of liquid sulphur present and were able to work only at one temperature, namely 445°C. Since the change in pressure occurring at this temperature is very small the results, which show an average deviation from the mean of 26 per cent may be regarded as quite satisfactory. Randall and Bichowsky[1] investigated the equilibrium in this system at temperatures above 880°C., where appreciable amounts of hydrogen are present at equilibrium. On the first page of their paper a brief footnote makes the following statement: "A mixture of moist SO_2 and H_2S when passed through a clean glass tube at 60°, deposited but little sulphur. However, when the tube was etched, sulphur was deposited rapidly at the same temperature." This is the only indication in the literature of the true nature of the reaction.

Experiment

The kinetics of the reaction were studied by a dynamic method. The work of Lewis, Randall and Bichowsky demonstrated the difficulty of applying static methods to this system. The gases were allowed to flow at a constant rate through a reaction chamber kept at constant temperature. Determinations of the composition of the gases leaving the chamber permitted the calculation of the rate at which reaction was proceeding. The temperature coefficient was determined through a range of temperatures for two reaction chambers, equal in volume, but of widely different surface area. The effect of variation of partial pressures of the reacting gases was then determined at constant temperature.

Hydrogen sulphide of 99.5 per cent purity can be readily prepared from calcium sulphide as recommended by Pollitzer.[2] Kahlbaum's chemically pure calcium sulphide in lump form was used in an ordinary Kipp generator with a solution of hydrochloric acid. Before connecting the generator to the remainder of the apparatus about four liters of H_2S were drawn off to ensure the removal of all air. The gas then generated was completely absorbable in 20 per cent sodium hydroxide.

The sulphur dioxide was taken from a cylinder of commercial liquid SO_2 Half of the original contents had been withdrawn, thus removing any air present. Each gas was passed over phosphorus pentoxide before entering the reaction chamber.

In order to obtain accurate measure of the rate of flow of a gas by means of a flow-meter a very steady pressure must be maintained. For this purpose a second Kipp generator containing distilled water was connected to the first and used as a gasometer. A three-way stopcock was used at the mouth of the gasometer so that it could be permanently connected with both the generator and the hydrogen sulphide flow-meter. Since the gasometer contained water it also served to remove all traces of hydrogen chloride carried over from the

[1] J. Am. Chem. Soc., **40**, 368 (1918).
[2] Z. anorg. Chem., **64**, 121 (1909).

generator. The sulphur dioxide gasometer contained concentrated sulphuric acid and was similarly connected with the cylinder of liquid sulphur dioxide and the sulphur dioxide flow meter.

The flow-meters were of the type described by Benton[1] for very small rates of flow. The capillaries were about one centimeter in length, blown in Pyrex. Distilled water was used in the manometers and was of course saturated with the gas passing through the flow-meter.

From its flow-meter each gas was passed through a large Pyrex U-tube containing phosphorus pentoxide. These drying tubes were sealed directly to the remainder of the apparatus which was entirely of Pyrex. From the drying tube each gas was passed through a stopcock lubricated with meta-phosphoric acid. The gases were then mixed and passed directly into the reaction tube. A coil of Pyrex tubing of five millimeters bore joined to a test tube furnished the first reaction tube, which had a volume of 56 cc. and an inner surface area of approximately 320 sq. cm. Reaction tube 2 was blown from two test tubes giving a resultant volume of 51 cc. and surface area of 120 sq. cm.

The reaction tube was maintained at constant temperature in an electric furnace whose inside dimensions were 15 cm. in length by 7 cm. in diameter. The top of the furnace was well insulated with an asbestos board 1.5 cm. in thickness through which the glass tubes connected with the reaction tube and also the thermocouple wires were passed. The current through the furnace windings was controlled by a small rheostat. The temperature was measured by a Hoskins pyrometer, the thermocouple being cemented to the furnace cover so that it occupied the same position in the furnace in each experiment.

The success of this method of determining the extent of reaction depends mainly upon the manner of treatment of the gases coming from the reaction tube. In general, rapid cooling is necessary in order to prevent further reaction but with the system under discussion the gases flowing from the reaction tube cannot be cooled to room temperature. The reason for this is one which all previous investigators failed to observe. If but one droplet of water be allowed to condense in the presence of hydrogen sulphide and sulphur dioxide these gases proceed to react very rapidly in the solution thus formed. Their interaction results in the production of sulphur and more water. However, it was found that cooling to 100°C. effectively stopped the reaction, permitted the complete condensation of the sulphur vapor formed in the reaction tube, and prevented the condensation of moisture. A bulb about 5 cc. in volume was blown in the exit tube at the point at which it projected from the furnace covering. Here the condensed sulphur was permitted to collect. A Pyrex tube 8 cm. in length was sealed to the bulb and was ground at the end to fit the mouth of an absorption bulb. The sulphur bulb and its tube were surrounded by a housing of sheet asbestos which enclosed a 100 watt electric light bulb. The temperature of the enclosure was thus regulated between 100° and 110°C. using a rheostat in series with the lamp.

[1] J. Ind. Eng. Chem., **11**, 623 (1919).

The absorption tube was designed to obtain complete absorption without bubbling. Any type of bulb permitting even slight fluctuations in pressure caused by bubbling of the gases through the absorbing liquid rendered the manometer readings of the flow-meters uncertain. Two closed cylindrical bulbs of 1 cm. diameter and 6 cc. volume were connected at one end by a short piece of small tubing so that they were parallel and 1 cm. apart. At the other end one bulb carried a short open tube of 2 mm. bore, while the other bulb terminated in a tube ground to fit the exit of the main train of apparatus and bent so that the absorption bulbs assumed a horizontal position when connected to the exit. In this position a large surface of absorbing liquid was exposed to the gases entering the bulb, and since they dissolve rapidly and completely in that solution, no bubbling could take place.

Each flow-meter was calibrated by absorbing, in 30 per cent sodium hydroxide solution, all the gas passing through it during a definite time interval at various readings of the manometer. The time interval was made long enough to give an increase in weight of the absorption bulb of from 0.15 to 0.2 g. A calibration curve for each flow-meter was made by plotting difference in manometer levels against grams of gas per minute. These curves were checked once a week at several different rates of flow.

The reaction tube was cleaned with a chromic acid cleaning solution and washed well with distilled water. After it was placed in the furnace and sealed to the remainder of the apparatus it was dried at 500°C. with a slow stream of dry sulphur dioxide over-night. This procedure was also of the nature of a heat treatment, since comparable reaction velocities could not be obtained with a fresh tube. It was further found necessary to allow the reaction to proceed for eight or nine hours within the tube before its condition became fixed and duplicate results could be obtained.

The next step was to bring the furnace to the desired temperature at which it was maintained by manual operation of the furnace rheostat within $\pm 1^{\circ}$ throughout the run. The rate of flow of gases was kept constant by frequent manipulation of stop-cocks. After attaching the weighed absorption bulb in order to make a run, the stop-cocks were not touched since it was found that greater accuracy was achieved by averaging the initial and final readings of the flow-meter manometers during the run. For each run there were recorded initial and final values of the following: time, temperature, the two manometer levels in each flow-meter and the weight of the absorption bulb.

In experiments 1 and 2 at all temperatures below 580°C. the rate of reaction showed a gradual change with time for a period of from 2 to 3 hours. Only when a constant rate of formation of sulphur had finally been reached and several runs differed no more than one per cent from the mean, was the experiment at this temperature discontinued.

The results of experiments 1 and 2 show that the reaction takes place almost entirely on the surface of the reaction tube. Therefore experiment 3 was performed at constant temperature with constant total volume of gas entering the reaction tube but with various partial pressures of hydrogen sulphide and sulphur dioxide.

Calculations and Results

The rate at which H_2S and SO_2 entered the reaction tube was obtained from the average manometer readings by reference to the calibration curves where rates were plotted in grams per minute. A portion of the gas mixture reacted to produce sulphur, which condensed out completely in the sulphur bulb, and water which passed on into the absorption bulb. The increase in weight of the latter is therefore equal to the weight of unchanged H_2S and SO_2 plus that of the water formed. The difference between the total weight of H_2S plus SO_2 which entered the reaction chamber during a run and the increase in weight of the absorption bulb represents the amount of sulphur formed. If this difference be divided by the duration of the run the rate of formation of sulphur is obtained in grams per minute.

It was found in experiment 3 that the rate of the reaction as represented by the rate of formation of sulphur depends upon the partial pressures of the reactants according to the following equation:

$$K = \frac{S}{P_{H_2S}^{1.5} \quad P_{SO_2}}$$

where K is the velocity constant, S is the number of grams of sulphur formed per minute, P_{H_2S} is the average partial pressure of the hydrogen sulphide and P_{SO_2} that of the sulphur dioxide.

In order to calculate the average partial pressure of each reactant it is necessary to determine both the initial partial pressures and those after reaction has taken place to the extent necessary to form S grams of sulphur per minute. The latter calculation is complicated by the dissociation of the molecules of sulphur vapor into S_8, S_6, and S_2 molecules. The excellent work of Preuner and Schupp[1] on the dissociation of sulphur vapor furnishes the data necessary to compute the average molecular weight of sulphur vapor at various temperatures and at partial pressures between 0 and 180 mm. The latter limit is high enough to include the range of partial pressures produced under the conditions of the experiments being described. These average values were plotted against the corresponding temperatures. This afforded a means of interpolation to intermediate temperatures. Fortunately the error involved in estimating the vapor density of sulphur decreases as the temperature is increased and it is at the higher temperatures only that the volume of sulphur produced becomes large.

The partial pressures of the constituents of a mixture of gases vary but little with change in temperature. It was convenient therefore, to reduce all calculations of partial pressure to normal temperature and pressure, taking care however, to use the value for the molecular weight of sulphur vapor corresponding to the temperature of the experiment.

The data obtained in experiment 2 at 621°C. are the basis of the following computations:

[1] Z. physik. Chem., **68**, 129 (1910).

Experimental Data

Temp.	Time	Wt. H_2S/min.	Wt. SO_2/min.	Wt. absorbed
621°C.	10 min.	0.01105g.	0.01049 g.	0.1317 g.

Computations

Total Wt. reactants = $0.02154 \times 10 = 0.2154$ g.
Total Wt. sulphur = $0.2154 - 0.1317 = 0.0837$ g.
Wt. sulphur per min. = S = 0.00837 g.
Hereafter all volumes are per minute.

$$\text{Vol. } H_2S = \frac{\text{Wt. } H_2S \text{ per min.} \times 1000}{\text{Wt. Liter } H_2S} = \frac{.01105 \times 1000}{1.5392} = 7.179 \text{ cc.}$$

$$\text{Vol. } SO_2 = \frac{\text{Wt. } SO_2 \text{ per min.} \times 1000}{\text{Wt. Liter } SO_2} = \frac{.01049 \times 1000}{2.9267} = 3.584 \text{ cc.}$$

Total Vol. reactants = 10.763 cc.
Initial $P_{H_2S} = 0.667$ atmos.
Initial $P_{SO_2} = 1 - P_{H_2S} = 0.333$ atmos.

$$\text{Vol. } H_2S \text{ reacted} = S \times \frac{2 \text{ Mol. Wt. } H_2S}{3 \text{ At. Wt. S}} \times \frac{1000}{\text{Wt. Liter } H_2S}$$
$$= 3.854 \text{ cc.}$$

Therefore Final Vol. $H_2S = 7.179 - 3.854 = 3.325$ cc.
Similarly Final Vol. $SO_2 = 1.679$ cc.

$$\text{Vol. S formed} = \frac{S \times 22400}{\text{Mo. Wt. S at } 621^\circ} = 2.678 \text{ cc.}$$

Vol. H_2O formed = 3.899 cc.
Final Total Vol. = Final Vol. $H_2S + SO_2 + S + H_2O$
= 11.581 cc.
Hence Final $P_{H_2S} = 0.287$ atmos.
Final $P_{SO_2} = 0.145$ atmos.

$$\text{Average } P_{H_2S} = \frac{\text{Initial} + \text{Final}}{2} = 0.477 \text{ atmos.}$$

Average $P_{SO_2} = 0.239$ atmos.
$P_{H_2S}^{1.5} = (0.477)^{1.5} = 0.330$

$$\text{Hence} \quad K = \frac{S}{P_{H_2S}^{1.5} \times P_{SO_2}} = 0.1061$$

Results

G = Increase in weight of absorption bulb.
S = Number of grams of sulphur formed per minute.
P_{H_2S} = Average partial pressure of H_2S
P_{SO_2} = Average partial pressure of SO_2
K = Velocity Constant = $S/(P_{H_2S}^{1.5} \times P_{SO_2})$
T = Absolute Temperature

EXPERIMENT 1

Reaction tube 1. Volume 56 cc. Surface area 317 sq. cm.

	Temp. °C	Time Min.	Grams H_2S / Min.	Grams SO_2 / Min.	G	$S \times 10^5$
1.	371	10	0.01097	0.01033	0.1885	245
2.	406	10	0.01093	0.01029	0.1705	417
3.	430	10	0.01120	0.01038	0.1623	535
4.	452	10	0.01092	0.01055	0.1501	646
5.	471	10	0.01110	0.01043	0.1418	735
6.	475	10	0.01116	0.01044	0.1400	760
7.	510	10	0.01111	0.01045	0.1252	904
8.	539	10.9	0.01100	0.01046	0.1293	960
9.	571	10	0.01107	0.01031	0.1149	989

	Mol. Wt. Sulphur	$P^{1.5}_{H_2S}$	P_{SO_2}	$K \times 10^4$	log K	$1/T \times 10^4$
1.	203	0.493	0.309	160	−1.796	15.53
2.	180	.451	.291	318	−1.498	14.73
3.	165	.429	.277	450	−1.347	14.22
4.	152	.389	.273	608	−1.216	13.79
5.	140	.375	.257	762	−1.118	13.44
6.	137	.370	.254	809	−1.092	13.37
7.	116	.333	.238	1139	−0.943	12.77
8.	100	.312	.231	1331	−0.876	12.32
9.	85	.301	.222	1481	−0.829	11.85

EXPERIMENT 2

Reaction tube 2. Volume 51 cc. Surface area 121 sq. cm.

	Temp. °C	Time Min.	H_2S / Min.	SO_2 / Min.	G	$S \times 10^5$
10.	438	10	0.01108	0.01026	0.1905	229
11.	484	10	.01101	.01033	.1754	380
12.	521	13	.01101	.01054	.2077	557
13.	550	10	.01094	.01044	.1487	651
14.	583	10	.01100	.01040	.1376	764
15.	621	10	.01105	.01049	.1317	837
16.	666	10	.01100	.01025	.1203	922
17.	688	10	.01098	.01038	.1173	963
18.	725	10	.01100	.01032	.1088	1044
19.	733	10	.01111	.01041	.1091	1061

EXPERIMENT 2 (Continued)

	Mol. Wt. Sulphur	$P^{1.5}_{H_2S}$	P_{SO_2}	K × 10⁴	log K	1/T × 10⁴
10.	160	0.497	0.306	151	−1.821	14.06
11.	131	.457	.292	285	−1.545	13.21
12.	110	.406	.277	495	−1.305	12.59
13.	95	.379	.264	650	−1.187	12.15
14.	80	.350	.248	880	−1.055	11.68
15.	70	.330	.239	1061	−0.974	11.19
16.	66	.312	.225	1313	−0.882	10.65
17.	66	.301	.224	1429	−0.845	10.41
18.	65	.285	.213	1720	−0.765	10.02
19.	65	.284	.213	1754	−0.756	9.69

EXPERIMENT 3

Reaction Tube 2. Volume 51 cc. Surface area 121 sq. cm.
Temperature 480°C.

Molecular weight of Sulphur for partial pressures from 0 to 100 mm. = 124.

TABLE I

	Time Min.	Grams H_2S / Min.	Grams SO_2 / Min.	G	S × 10⁵	P_{H_2S}	P_{SO_2}
21.	10	0.01335	0.00587	0.1585	337	0.744	0.153
22.	10	.01335	.00610	.1591	354	.735	.157
23.	10	.01270	.00733	.1617	386	.689	.193
24.	12	.01276	.00744	.1943	401	.685	.194
25.	10	.01172	.00918	.1674	416	.625	.249
26.	10	.01175	.00925	.1666	434	.619	.149
27.	10	.01065	.01078	.1700	443	.561	.302
28.	10	.01072	.01084	.1690	466	.557	.300
29.	10	.00964	.01320	.1821	463	.486	.368
30.	11	.00961	.01323	.2014	453	.486	.375
31.	12	.00953	.01328	.2201	447	.485	.379
32.	10	.00851	.01544	.1970	425	.424	.447
33.	10	.00636	.01939	.2232	343	.313	.584
34.	11	.00635	.01933	.2471	354	.310	.582
35.	10	.00639	.01937	.2215	361	.310	.581

TABLE II

$$K_1 = \frac{S}{P_{H_2S}^2 P_{SO_2}} \qquad K_2 = \frac{S}{P_{H_2S} P_{SO_2}^{0.5}} \qquad K_3 = \frac{S}{P_{H_2S}^{1.6} P_{SO_2}}$$

$$K = \frac{S}{P_{H_2S}^{1.5} P_{SO_2}} \qquad K_4 = \frac{S}{P_{H_2S} P_{SO_2}^{0.78}} \qquad K_5 = \frac{S}{P_{H_2S} P_{SO_2}}$$

$10^4 \times$	K_1	K_2	K_3	K	K_4	K_5
21.	398	116	353	343	196	296
22.	417	125	369	357	204	307
23.	421	128	363	350	202	290
24.	441	133	379	365	211	302
25.	428	133	355	338	219	267
26.	455	141	376	358	205	282
27.	466	143	369	349	201	262
28.	501	153	396	373	214	279
29.	533	157	417	371	208	259
30.	511	153	384	356	200	249
31.	501	149	376	349	196	243
32.	529	140	376	344	188	224
33.	599	144	377	336	167	188
34.	633	149	395	351	174	196
35.	647	153	405	359	178	200
Average	499	141	379	353	196	256
Average Deviation	12.4%	6.8%	3.7%	2.5%	12.4%	12.4%

Errors.

Lewis and Randall[1] determined the equilibrium constant at 445°C. for the reaction

$$2H_2S + SO_2 = 3S(l) + 2H_2O + Q \text{ calories}$$

at constant partial pressure of sulphur to be

$$K_P = \frac{P_{H_2O}^2 P_{S_6}^{0.5}}{P_{H_2S}^2 P_{SO_2}} = 649$$

The variation of K_P with temperature depends upon Q in accordance with the van't Hoff isochore

$$\frac{d \ln K_P}{dT} = \frac{-Q}{RT^2}$$

To prove that the above K_P is less than that at all temperatures below 445° it is only necessary to show that Q is positive. The following heats of formation are given by Lewis:

[1] Lewis and Randall: "Thermodynamics" (1923).

$3S(l)$ from $3S$(rhombic) $= -1401$ calories
$2H_2O(g)$ from $O_2(g)$ and $2H_2(g) = 105640$ calories
$2H_2S$ from S(rhombic) and $2H_2(g) = 9520$ calories
SO_2 from S(rhombic) and $O_2(g) = 69000$ calories

The value of Q is therefore 105640 − 1401 − 9520 − 69000, that is, 25719 calories. Below 445° the amount of S_2 in the vapor phase is negligible and the exponent of P_S varies from about ½ to about 3/8.

Not only does the value of K_P increase as the temperature is lowered, but the saturation value of P_S rapidly diminishes. These facts indicate that the product $P^2_{H_2S}\, P_{SO_2}$ at equilibrium must diminish very rapidly with decrease in temperature. Since each of the partial pressure values in the equilibrium equation is less than one atmosphere, the product $P^2_{H_2O}\, P^n_S$ is always much less than one. Therefore the product $P^2_{H_2S}\, P_{SO_2}$ must always be much less than $1/K_P = 0.00154$. Under the conditions of the experiment the value of $P^2_{H_2S}\, P_{SO_2}$ in the exit gases was in no case less than 0.003.

This result proves that it is impossible for the sulphur condensing at the exit of the reaction chamber to react with the water vapor in the exit gases.

The sulphur bulb was maintained at a temperature of between 100° and 110°C. The vapor pressure of sulphur at 110°C. is 0.0136 mm.[1] The molecular weight of sulphur vapor at 110°C. is 256. The weight of 1 cc. is therefore 0.00083 g. The most rapid rate at which the gases entered the absorption bulb was 14.7 cc. per minute. The weight of sulphur carried into the absorption bulb per minute was therefore $0.0136/760 \times 14.7 \times 0.00083 = 0.000002$ g. The total weight per run of ten minutes duration was 0.00002 g.

The solubility of hydrogen sulphide in liquid sulphur reported by Pélabon[2] introduced no appreciable error. The amount dissolved increases with rise in temperature and even at 440°C. is but 0.3 cc. = 0.00045 g. per gram of sulphur. At most only 0.1 g. of sulphur was formed during a run.

The fact that the reaction took place mainly on the surface of the reaction tube eliminates the possibility of the introduction of error due to reaction during the cooling of the gases from the temperature of the reaction tube to that of the sulphur bulb. The amount of surface in the exit tube whose temperature lay between that of the reaction tube and 110° was certainly less than 6 sq. cm. With reaction tube 1 whose surface was about 317 sq. cm. no measurable reaction took place at 180°C. It was also found that the condensation of sulphur in the sulphur bulb had no measurable effect upon the reaction velocity.

There seem, therefore, to be no inherent errors, so that the accuracy of the results depends upon the errors made in measurement and calculation. A consideration of the errors in the measurement of time, temperature, weight of gas absorbed and rate of flow of reactants showed that the precision was such as would lead to an average deviation of 2.5 per cent in the value of K, the velocity constant.

[1] Gruener: J. Am. Chem. Soc., **29**, 1396 (1907).
[2] Compt. rend., **124**, 35 (1897).

Discussion of Results

1. *The Heterogeneity of the Reaction.*

The results of experiments 1 and 2 are given graphically in Fig. 1. The values of log $_{10}$K are plotted as abscissae against the corresponding values of 1/T as ordinates. At 435°C., where $1/T = 14.12 \times 10^{-4}$, log K for the reaction tube 1 is -1.315 and for tube 2 is -1.850. Therefore the reaction proceeded 3.4 times as fast in tube 1 as in tube 2. At 571° this ratio becomes 1.9. In the mean the reaction occurred 2.7 times as fast in tube 1 as in tube 2. The ratio of their surface areas was 317 to 121 or 2.6. This proportionality

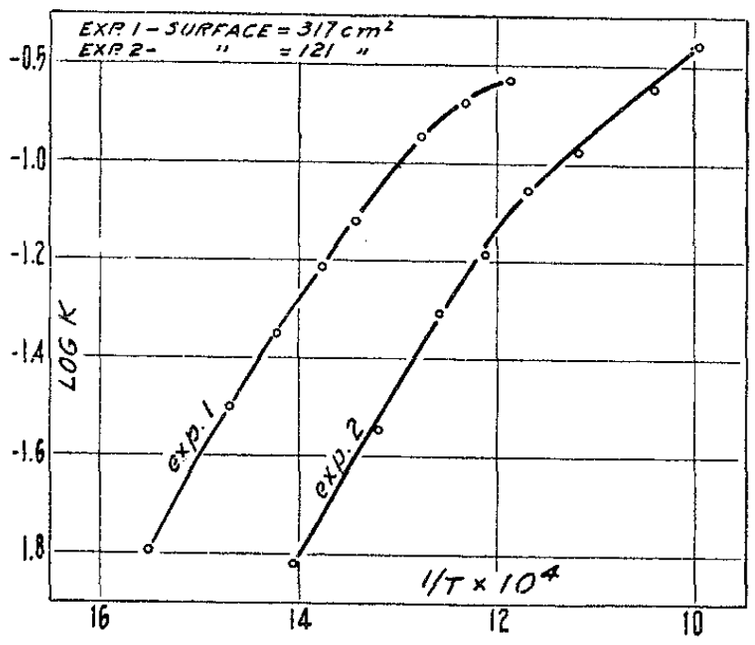


FIG. 1

of reaction velocity to surface is definite evidence that there can be little reaction between H_2S and SO_2 in the gas phase. The volumes of the two tubes were almost equal at 56 and 51 cc. respectively.

2. *The Temperature Coefficient.*

The variation of the velocity constant of a chemical reaction with temperature may be expressed by the Arrhenius equation: $d \ln K/d T = E/RT^2$ or in the integrated form:

$$\log K_2/K_1 = E/4.57(1/T_1 - 1/T_2)$$

When T_1 and T_2 are temperatures 10° apart, the value of K_2/K_1 is called the temperature coefficient of the reaction velocity. The values so calculated are given in the following table:

	Experiment 1		Experiment 2	
Temp. °C	Temp. Coef.	E Cal./Mol.	Temp. Coef.	E Cal./Mol.
370	1.239	17600	——	——
400	1.169	14000	——	——
435	1.151	14000	1.170	15600
475	1.134	14000	1.151	15600
510	1.076	8900	1.137	15600
550	1.037	4900	1.093	11900
600	——	——	1.058	8500
680	——	——	1.045	8000

The values of E thus calculated are probably not equal to the actual heats of activation of the chemical reaction involved. The amounts of reacting substances adsorbed on the surface of the vessel and therefore actually participating in the reaction, undoubtedly decrease with a rise in temperature. This would make the apparent value of E, calculated from the observed temperature coefficient, smaller than the true value which measures the actual stability of the adsorbed molecule.

It can be seen that the temperature coefficient decreases with increase in temperature. At lower temperatures it is comparatively high, then decreases steadily. This variation is in accord with the theory that the reaction velocity depends upon the amount of reactants adsorbed, the resultant temperature coefficient being equal to the sum of the negative temperature coefficient of adsorption and the positive coefficient of the chemical reaction. There are no data available which show the heats of adsorption of SO_2 and H_2S on glass at high temperatures. The magnitude of the effect of temperature on the adsorption of these gases cannot be estimated, so that the true heat of activation for the reaction between H_2S and SO_2 on glass surfaces cannot yet be calculated.

The fact that the temperature coefficients of the reaction were different at a given temperature for the two reaction vessels used is probably due to a slight difference in the surfaces. It may be that only the SiO_2 groups of the surface are active in adsorption of H_2S or SO_2, or that only the Na_2O groups can activate these gases. Again it may be that each of these groups activates one of the reactants. Further study of the adsorptions may determine the exact details of the mechanism at the surface. It is remarkable indeed, in view if the recent work of Hinshelwood on the decomposition of formic acid[1], that the curves of log K against 1/T are so nearly parallel. Hinshelwood found that the velocity of the decomposition of formic acid and the relative ease with which it follows the two alternative paths of reaction to form $H_2 + CO_2$ or $H_2O + CO$ are very sensitive to the nature of the glass surface. At 300°C. for example, the amounts of $CO_2 + H_2$ in the products of formic acid decomposition on equal surface areas were:

[1] Proc. Roy. Soc., **100** A, 575 (1922); J. Chem. Soc., **121**, 1668 (1922); **123**, 1014, 1333 (1923).

Duro glass	74%	73%	63%
Soda glass	19.1%	18.3%	16.5%

Duro glass is similar in composition to pyrex glass.

3. *Mechanism of the Reaction.*

Examination of the results tabulated for experiment 3 shows immediately that the rate of formation of sulphur is directly proportional to some power of the partial pressure of each of the reactant gases. This suggests that both gases are adsorbed and only adsorbed molecules react. If but one of the gases is adsorbed and reaction takes place when a molecule of the other gas collides with an adsorbed molecule, there is a range of pressures through which the reaction velocity is independent of the partial pressure of the adsorbed type of gas. In this range the surface of the catalyst is saturated with adsorbed gas and the velocity depends upon the number of molecules of the unadsorbed type which strike the surface. At constant temperature, the rate at which the molecules of a given gas strike a plane surface is directly proportional to the pressure of the gas. Langmuir[1] found that at high temperatures the surface of platinum in a mixture of carbon monoxide and oxygen is nearly covered with oxygen, and the velocity is then limited by the rate at which the monoxide strikes the surface.

If both the gases are adsorbed and only one is activated by the adsorption, the reaction velocity will be directly proportional to the fraction of surface covered by the activated gas, and inversely proportional to the fraction of surface covered by the inert gas. The results obtained by Bodenstein and Ohlmer[2] on the oxidation of carbon monoxide on quartz, in which case the adsorbed carbon monoxide is inert, and the results of Bodenstein and Fink[3] on the oxidation of sulphur dioxide, in which case the adsorbed SO_3 is inert, indicate just such a mechanism.

The results of experiment 3 are best explained by assuming that both the H_2S and SO_2 are adsorbed and that reaction takes place only between these adsorbed molecules. If this is indeed the case, then the reaction velocity would be proportional to the fraction of surface covered by groups consisting of one SO_2 and two H_2S molecules situated adjacently. The probability of this condition occurring is proportional to the product of the square of the fraction of surface covered by H_2S times the fraction of surface covered by SO_2. Let F_{H_2S} equal the fraction of surface covered by H_2S and F_{SO_2} the fraction covered by SO_2 molecules. Then the velocity will be given by:

$$S = k F^2_{H_2S} F_{SO_2}$$

The fraction of surface covered by an adsorbed gas is given by the Freundlich isotherm:

$$F = a P^{1/n}$$

[1] Trans. Faraday Soc., **17**, 621 (1921).
[2] Z. physik. Chem., **53**, 175 (1905).
[3] Z. physik. Chem., **60**, 1 (1907).

Therefore, $$F_{H_2S} = k_1 P_{H_2S}^{1/n}$$

$$F_{SO_2} = k_2 P_{SO_2}^{1/m}$$

Substituting, $$S = K P_{H_2S}^{2/n} P_{SO_2}^{1/m}$$

The adsorption of H_2S on glass surfaces has not yet been studied. Therefore the value of 1/n is not known. Bangham and Burt[1] have studied the adsorption of SO_2 on glass quite recently but their research "brought to light a conspicuous difference in the behavior of SO_2 from that of any gas previously tested" (N_2O, NH_3 and CO_2). Continued heating in vacuo at 200°C. did not remove all the adsorbed SO_2 so that they were unable to evaluate the pressure exponent. However, McGavack and Patrick[2] found that for SO_2 adsorbed by silica gel the value of 1/m is 0.485 at 30°C., 0.533 at 57°, 0.662 at 80° and 0.745 at 100°C. If these values be extrapolated it will be seen that the value of 1/m approaches 1 asymptotically at about 150°C. It seems reasonable therefore, to conclude that the value in the above expression at temperatures above 350°C. is nearly 1.

The value of 2/n must lie somewhere between 2 and 0. Various exponents for P_{H_2S} lying in this range were used in calculating velocity constants and the results are tabulated in experiment 3, Table II. It will be seen that the smallest average deviation is obtained where 2/n = 1.5. This indicates that the pressure exponent for hydrogen sulphide at 480°C. is about 0.75. At high temperatures the pressure exponents of adsorption vary but slowly with temperature.

Very few data have yet been determined on reactions at catalyst surfaces where both reactants are adsorbed and activated. None are available for any reaction of the same type as the one studied, where the reaction is apparently trimolecular and both gases activated by adsorption. Pease[3] found that the velocity of combination of ethylene and hydrogen at copper surfaces could be expressed by an equation

$$K = \frac{dP/dt}{V_{H_2}^{0.80} V_{C_2H_4}^{0.66}}$$

where dP/dt = rate of decrease of pressure

V_{H_2} = initial volume of hydrogen

$V_{C_2H_4}$ = initial volume of ethylene.

The mechanism of this reaction is quite similar to the H_2S-SO_2 reaction but it is bimolecular and hence simpler.

Summary

1. Measurements have been made of the velocity of combination of hydrogen sulphide and sulphur dioxide in Pyrex reaction tubes at temperatures ranging from 370 to 730°C. The velocity was found to be proportional to the surface area of the reaction chamber, which proves that the glass surface

[1] J. Phys. Chem., **29**, 548 (1925).
[2] J. Am. Chem. Soc., **42**, 946 (1920).
[3] J. Am. Chem. Soc., **45**, 2235 (1923).

acts as a contact catalyst for the reaction. Further the temperature coefficient was found to decrease with a rise in temperature.

2. Measurements of the velocity at constant temperature show it to vary directly as the partial pressure of the sulphur dioxide and as the partial pressure of the hydrogen sulphide raised to the 1.5 power.

3. A mechanism of reaction in harmony with the modern theories of heterogeneous reactions has been suggested, and substantiated by the results. According to this mechanism each of the reactants is activated by adsorption on the surface of the glass and reaction then follows between the activated molecules only.

New York, N. Y.

-50

AN IMPROVED DYNAMIC METHOD FOR MEASURING VAPOR PRESSURES

J. N. PEARCE AND R. D. SNOW

In the study of the colligative properties of solutions use may be made of methods involving the lowering of the freezing point, the lowering of the vapor pressure and the elevation of the boiling point of the solvent by the solute, and the application of electromotive force methods. Because of the ease and the accuracy of the measurements most of the work, hitherto, has been confined to the application of the freezing point and electromotive force methods. Both the freezing point and the boiling point methods are of limited application because of the fact that they can be used accurately only for a narrow temperature interval. The latter method is further handicapped for the reason that we have no accurate specific heat data for liquids at temperatures near their boiling points. While the electromotive force methods may be used at any temperature, they are limited to only those cases for which perfectly reversible electrodes are obtainable.

Of all the properties of solutions none are more accessible to thermodynamic treatment than the vapor pressure. While the method is free from all of the disadvantages of the above mentioned methods and in addition offers many advantages, the results obtained have not been all that could be desired.

Four general methods have been employed for measuring the vapor pressures of solvents and solutions. They are: (1) static, (2) indirect, (3) differential, and (4) dynamic.

The static method has been used by many investigators, including Wüllner[1] and Raoult[2]. In principle, this method consists essentially in placing the liquid whose vapor pressure is to be determined above the mercury in a Torricellian vacuum and comparing the height of the mercury with that in another barometer tube at the same temperature. Tammann[3] has shown, however, that the method is open to serious errors due to small traces of air and volatile impurities unavoidably present in the solution and on the sides of the tubes. Furthermore, there is no assurance that the concentration of the solution remains uniform throughout.

The indirect method, as perfected by Ramsay and Young[4], consists in observing the temperatures at which solutions boil under various pressures. They have used the method extensively and their results on the vapor pressure of water above 100° are still accepted as standard. Emden[5], and Holborn

[1] Wüllner: Pogg. Ann., **103**, 529 (1856); **110**, 564 (1860).
[2] Raoult: Z. physik. Chem., **2**, 353 (1888).
[3] Tammann: Wied. Ann., **33**, 322 (1888).
[4] Ramsay and Young: Phil. Trans., **183A**, 107 (1892).
[5] Emden: Wied. Ann., **31**, 145 (1897).

and Henning[1] have used the method to measure the vapor pressures of many aqueous solutions. The objections to the indirect method are: (1) the liquid and the vapor are both liable to become superheated; (2) in the case of solutions, the concentration is changed by the evaporation of the solvent, and (3) the method is limited by the fact that many solutes decompose on boiling.

The differential method involves the comparison of the vapor pressures of two solutions, or of one solution and the pure solvent, by means of a manometer or a flexible membrane, and it gives directly the vapor pressure lowering. It does not, however, give us any knowledge of the absolute value of the vapor pressure over either liquid phase. Dieterici[2] separated the vapor above two different liquids by a flexible metallic membrane and measured the difference in vapor pressure by the movement of this membrane as magnified by a long pointer. The apparatus is too complicated and inflexible for general application. Fraser and Lovelace[3] have developed a modification of the differential method by which the vapor pressure lowerings may be determined with extreme accuracy. They compare the vapor pressure of a solution with that of the pure solvent by means of a very sensitive Rayleigh manometer. With this apparatus they have been able to measure the vapor pressure lowerings in solutions of potassium chloride, mannite and lithium chloride at 20° with an accuracy of 0.001 mm., or less. The apparatus and its technique require extreme precaution in the preparation of air-free solutions and in keeping them in constant aggitation. The time consumed, which varies from several days to several weeks for a single determination of the vapor pressure lowering, makes the method impractical for any but the most refined work. Tower and Germann[4] have measured vapor pressure lowerings in aqueous and alcoholic solutions by means of a Morley gauge.

The dynamic, or air-saturation method of measuring vapor pressures, is based upon Dalton's Law of partial pressures. The essential features of the method as commonly used are: (1) a measured volume of air is saturated with vapor by passing it over the surface of, or bubbling it through the liquid contained in the saturator, (2) the weight of the solvent evaporated is determined by the loss in weight of the saturator, or by the gain in weight of an absorber which removes the solvent from the effluent air, and (3) the total pressure exerted by the gaseous mixture in contact with the liquid is obtained from barometer and manometer readings. From the data thus obtained the vapor pressure of the liquid may be calculated.

Regnault[5], the first to use the dynamic method, passed air through a flask containing a sponge saturated with the liquid, then through screens of moist silk fastened to frames. The water vapor in the effluent air was determined by absorption in sulphuric acid and subsequent weighing. Since

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[1] Holborn and Henning: Ann. Physik, (4) **26**, 833 (1908).

[2] Dieterici: Wied. Ann., **50**, 47 (1893); Ann. Physik, (4) **70**, 617 (1923).

[3] Fraser, Lovelace, and students: J. Am. Chem. Soc., **38**, 515 (1916); **42**, 1793 (1920); **43**, 102 (1921); **45**, 2930 (1923).

[4] Tower and Germann: J. Am. Chem. Soc., **30**, 1219 (1908); **36**, 2449 (1914).

[5] Regnault: Ann. Chim. Phys., (3) **15**, 129 (1845).

Regnault's time the apparatus employed has undergone many and varied changes. In the modification developed by Ostwald and later used by Walker[1], air is bubbled through two Liebig bulbs containing the solution, then through pure water, and finally through a U-tube containing pumice soaked with sulphuric acid. The air first saturates itself with vapor up to the vapor pressure of the solution and then takes up from the water the quantity of vapor necessary to comp' .e the saturation. Finally, the water is absorbed by sulphuric acid. From the loss in weight of the water bulb, which is proportional to the difference between the vapor pressures of the solution and solvent, and the gain in weight of the acid tube, the relative lowering of the vapor pressure of the solvent is calculated. With slight variations in the apparatus and technique the method has been used with more or less success by a number of investigators.

The Earl of Berkeley and Hartley[2] have concluded that the failure of the original Walker-Ostwald method is due to variations in the hydrostatic pressure in the several vessels. They also suggest that liquid spray is mechanically carried from the solution to the pure solvent. Both of these sources of error were eliminated by passing the air slowly over the surface of the liquid contained in specially designed tubes shaken by the oscillating platform upon which they were mounted. The time required to make a complete vapor pressure determination was about three days and they claim an accuracy of the order of five percent.

Derby, Daniels and Gutsche[3] have determined the vapor pressures of pure alcohol and pure water by passing a measured volume of air axially through two rotating spherical bulbs filled with glass beads and partially filled with the liquid. The volume of air was accurately measured by means of two bulbs, each holding exactly 1135 c.c. The method employed was found to be quite accurate and very rapid. While they usually used from 8 to 10 liters of air for each experiment, they found that as much as 50 liters of air can be passed through the solution in one hour without affecting the efficiency of the saturator or the absorber.

Washburn and Heuse[4] have measured the relative lowering of the vapor pressure for weight molal solutions of cane sugar. They used saturators similar to those used by Berkeley and Hartley, but passed the air in succession through the following train: The air, drawn by a constant level aspirator, passes first through a soda-lime tube and then into the water presaturator, where it is saturated with water vapor at about 50°. The air then passes into a condensation flask which is immersed in the thermostat and here it deposits most of its excess of moisture and enters the first saturator of the train slightly supersaturated. On emerging from this saturator it is in equilibrium with water at 25°. It then passes out of the thermostat through a tube which is

[1] Walker: Z. physik. Chem., **2**, 602 (1888).
[2] Berkeley and Hartley: Proc. Roy. Soc., **77**, 156 (1906).
[3] Derby, Daniels and Gutsche: J. Am. Chem. Soc., **36**, 793 (1914).
[4] Washburn and Heuse: J. Am. Chem. Soc., **37**, 309 (1915).

heated by a coil to about 30°. The warm air then passes at once through an absorber, A_1, where all of the moisture is removed. The perfectly dry air then goes through a second presaturator containing water at 25° where it takes up the bulk of the moisture necessary to bring it into equilibrium with the solution in the saturator, S_2. After passing through this saturator and its absorber, A_2, the perfectly dry air passes directly into the third saturator, S_3, which contains pure water. In the first and third saturators the equilibrium is always approached from opposite directions, thus giving a valuable check upon the experimental conditions. The absorbers are large; about 25 grams of water can be condensed and absorbed in one absorber. Although the apparatus is very large and apparently cumbersome, it is, nevertheless, capable of a high degree of accuracy. In the use of this apparatus the measurement of the volume of air is unnecessary, since the same volume of air passes in turn over the solution and over the solvent, and the weight of the water evaporated from each is determined by the gain in weight of its respective absorber. A single experiment extends over a period of 24 hours, and they claim that the results are accurate to less than 0.5 percent.

A survey of the vapor pressure data obtained by the dynamic method shows not only a wide variation in the values reported by different investigators for a single liquid, but also very frequently a considerable variation in the data given by a single investigator. The chief reasons for these deviations are few, but they have been difficult to overcome. As mentioned before, one of the main sources of error is due to our inability to measure accurately, and at the same time conveniently, the large volume of air required for a single determination. The error thus introduced will be greater or less depending upon the magnitude of the vapor pressure of the liquid studied. This difficulty has been practically eliminated by the method of Washburn and Heuse but the apparatus is almost too cumbersome from the standpoint of convenience and speed. It is also largely eliminated in the method of Derby, Daniels and Gutsche but their apparatus requires constant and immediate attention. Owing to the surface film effect any form of apparatus which requires the passing of air over the surface of the solvent or solution must present a large liquid surface. Moreover, the surface should be in constant motion. Forms of apparatus involving the bubbling of air through the liquid are obviously more compact, but they introduce errors for the reason that while a bubble may be saturated with the vapor in the depth of the liquid, it will expand on rising and may become unsaturated. Unless, therefore, the air passes over the surface of the liquid again it may leave the apparatus without becoming entirely saturated. Again the mathematical formulae which have been used, heretofore, have been complicated; slight errors of observation are highly magnified in calculating vapor pressures.

In the pages which follow we shall describe an apparatus and its technique which greatly improves the dynamic method and eliminates many if not all of the difficulties experienced in the past

Apparatus

To reduce the errors involved in measuring the large volume of gas passed through the liquid we have generated the gas electrolytically and we are able to calculate indirectly from the mass of silver deposited in the coulometer not only the actual volume of the gas, but also the total number of mols of hydrogen and oxygen. The final form of the apparatus is shown in Fig. 1. Six electrolytic gas cells, A, are connected in series through the silver coulometer,

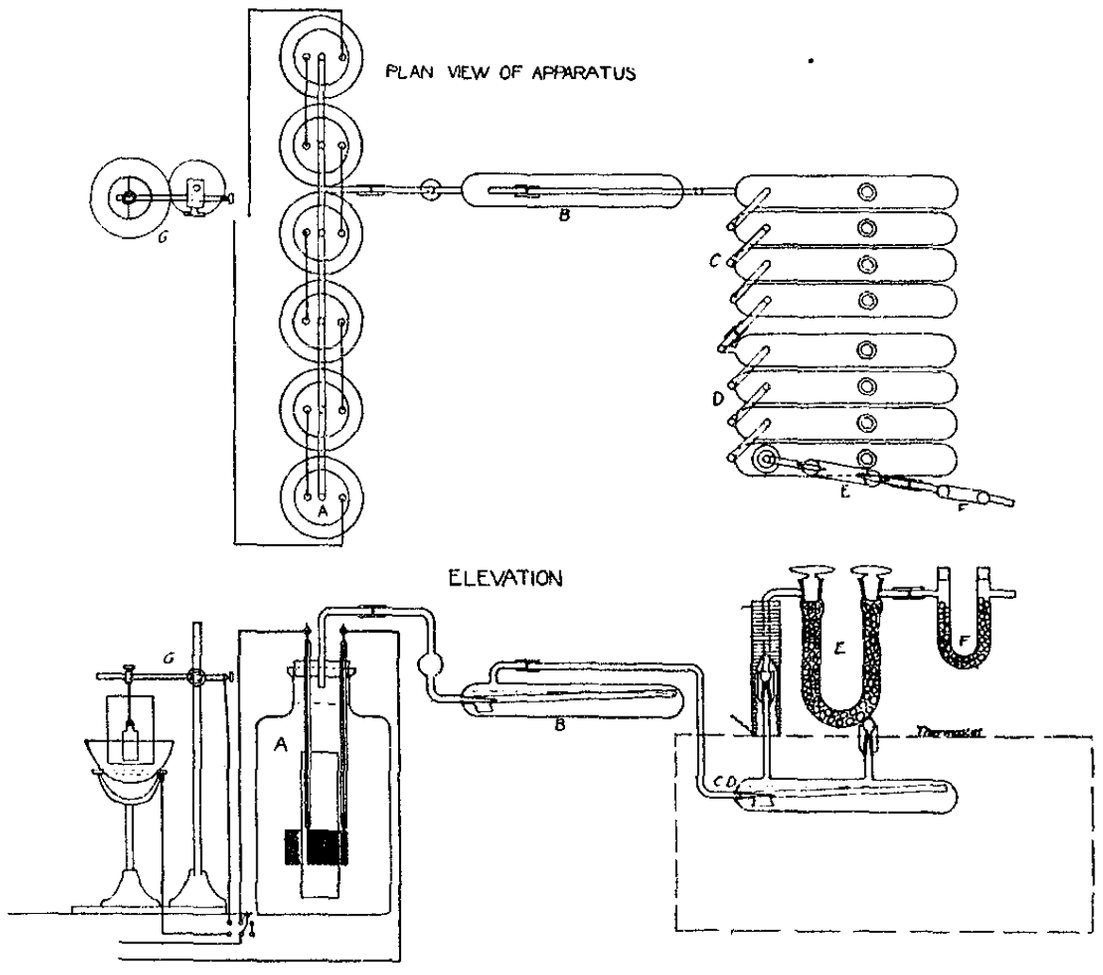


FIG. 1

S, with the laboratory storage battery system. The gases generated pass through a manifold tube into the presaturator, B, maintained at a few degrees higher than the bath temperature. From B the gases pass to the saturator, C, consisting of a battery of four saturation tubes sealed in series and containing pure conductivity water. In this way the moisture content of the gas is reduced to the normal saturation pressure at the temperature of the experiment. The gas then passes to a bank of four similar absorbers, D, containing the solution under investigation, where the vapor pressure falls to the normal vapor pressure of the solvent over the solution. Both C and D are immersed in a large Freas water thermostat maintained at 25° ± 0.002. Finally, the saturated gases pass through the absorber, E, and the protection tube, F, to the atmosphere.

Generators

The generators were wide mouth glass bottles of three and one-half liters capacity, each filled to the neck with a 25 percent solution of sodium hydroxide. The electrodes were of nickel wire gauze, each 3.5 by 9 inches, suspended by heavy nickel wire leads. The leads were inclosed by glass tubes passing through the rubber stopper. The tubes were fused to the wire at the bottom for a length of one inch, filled with melted paraffin and then sealed at the top with sealing wax to prevent leaks. The electrodes were separated by a glass cylinder extending through the middle two-thirds of the depth of the solution, thus preventing any possible recombination of the gases due to the catalytic influence of the nickel. The top of each electrolytic cell was hermetically sealed with De Khotinsky cement.

Saturators

The saturators were of the type used by Bichowsky and Storch[1]. The gases enter the bulb (Fig. 1. B) through a short central tube tapered down to a 2 mm. capillary. At the tip of the capillary the stream of gas breaks into bubbles which pass up a slightly inclined 5 mm. tube 10 inches long and then break at the end of the tube. An opening is blown through the lower side of this inclined tube just back of the tip of the capillary. Through this opening liquid is drawn from the bottom of the saturator and carried by the gas bubbles up the slanting tube to the surface of the liquid, thereby maintaining a practically uniform vapor concentration. The gas liberated from the bubbles as they burst then passes back over the surface of the liquid to an orifice leading either to a second saturator, or, finally, to the absorber, E. Each tube in a saturator, C or D, is provided with a vertical tube for filling and emptying. When the saturators are in use these tubes are closed by mercury seal stoppers.

This type of saturator has three distinct advantages over the Liebig bulb and the ordinary wash bottle type of saturators. They are: (1) each bulb introduces only a small hydrostatic pressure (about 1/2 inch of water), (2) after this pressure is released by the breaking of the bubble, the gas passes for some distance over the surface of the liquid, thereby having opportunity to come into equilibrium with the latter, and (3) the liquid is more efficiently stirred.

Absorber

The absorber consists of a six inch glass-stoppered U-tube joined by means of a mercury seal to the last bulb of the saturator D. The absorber contains glass beads which have been thickly coated with phosphorus pentoxide by rotating the beads in a bottle containing the oxide. This type of absorber exposes a large surface to the gases without offering any appreciable resistance to the flow. The protection tube F also contains beads similarly coated; this prevents moisture diffusing into the absorber from the atmosphere.

The silver coulometer used was of the porous cup type. The specifications proposed by Rosa and Vinal[2] were minutely followed. The electrodes were

[1] Bichowsky and Storch: J. Am. Chem. Soc., **37**, 2696 (1915).
[2] Rosa and Vinal: Bull. Bureau of Standards, **13**, 497 (1917).

supported by heavy glass rods set in iron stands. The anode was cast in the form of a cylinder from pure silver; the cathode was a platinum dish of 250 to 300 c.c. capacity. The porous cup was soaked in dilute nitric acid for several days, then distilled water was filtered through it, and it was finally heated at 130° to remove the last traces of acid. A solution of 15 grams of silver nitrate in 100 c.c. of water was used for the electrolyte.

The temperature of the bath was read from a normal glass thermometer, (B. S. No. 2‡577); the smaller fluctuations in temperature were indicated by means of a Beckmann thermometer immersed at the same point in the bath. Barometric pressures were read from a large precision barometer, readable by vernier to 0.05 mm. All pressures were reduced to 0°, sea level and 45° latitude.

Materials

Mannite. Pfanstiehl's "C. P." mannite was further purified according to the method of Brahme[1]. It was twice precipitated from distilled water and once from conductivity water by the addition of alcohol. After a second recrystallization it melted sharply at 166°. It was then dried and heated to constant weight at 125°-130°.

Potassium Chloride. A good "C. P." sample of the salt was twice recrystallized from pure distilled water and once from conductivity water. After drying, the salt was heated in a platinum dish until decrepitation ceased and then preserved in a desiccator over P_2O_5 until used.

Silver. The silver used as anodes was specially prepared and the analysis showed that it was 99.8 percent pure. It was further purified by electrolysis, then fused and cast in the form of cylinders. Chemically pure silver nitrate was twice recrystallized from dilute nitric acid solution and then repeatedly fused with excess nitric acid to remove organic impurities.

The various molal solutions of potassium chloride and mannite were made with water distilled from an alkaline permanganate solution and condensed in a block tin condenser.

Experimental

In order to avoid the evaporation and condensation of any solvent on the walls of the tube leading from the solution saturator, the current was turned through the coil surrounding the mercury seal. At the same time the direct current was switched through the electrolytic cells and gas was passed through the saturators for about one-half hour before the coulometer or the absorber were attached.

The absorber, E, was counterpoised on a sensitive balance by a similar U-tube filled with glass beads. After coming to equilibrium, one stopper of each tube was temporarily opened and the final weighing was made. A platinum dish cathode, previously cleaned, dried at 150° and cooled in a desiccator, was accurately weighed. All weighings were made by the oscillation method and are accurate to ±0.01 mg. At the end of the half hour period the switch to the generator was opened, the coulometer assembled,

[1] Brahme: J. Am. Chem. Soc., 41, 1707 (1919).

and the absorber and protection tube were put in place. The current was immediately switched through the whole system and the barometer reading was taken. Barometer readings were taken at frequent intervals throughout the experiment. At the end of the experiment the current was shut off and the absorber and protection tube were connected by another mercury seal to a long glass tube containing beads coated with P_2O_5, An aspirator was attached to F and dry air was drawn through the absorber to displace the gaseous mixture of hydrogen and oxygen, and to carry any vapor condensed on the side arm of the absorber into the absorber itself. Aspiration was continued for an hour, after which the absorber was removed, closed, wiped with clean dry chamois skin, and then allowed to stand in the tightly closed balance case over night. The final weighings were made with one stopcock open. Repeated aspiration of the absorber with dry air did not measurably change the final weight. At the completion of the experiment the electrolyte was siphoned from the platinum dish and the deposit was washed free from silver nitrate. The dish was then dried for an hour at 150°, cooled in a desiccator and weighed.

From the three data thus obtained, viz., the weight of the water evaporated, W_w, the weight of the silver deposited, W_s, and the corrected barometer pressure, P, the vapor pressure of the solution can be easily calculated by a direct application of Dalton's law. Thus, if the mixture of hydrogen, oxygen and water vapor are in equilibrium with the solution at the atmospheric pressure, P, (corr.), then the partial pressure of the water vapor, p, in the mixture will be proportional to its mol fraction. That is,

$$p = \frac{n_1}{n_1 + n_2} P,$$

where n_1 is the number of mols of water vapor and n_2 is the number of mols of hydrogen and oxygen combined. n_1 is calculated from the weight of water vapor collected in the absorber and the molecular weight of water, thus $n_1 = W_w/18.016$. n_2 is obtained from the weight of silver deposited in the coulometer. While the electrochemical reaction:

$$2\ Ag^+ + 2\ (e) \longrightarrow 2\ Ag\ ,$$

is taking place at the coulometer cathode six mols of hydrogen and three mols of oxygen are being liberated in the six generators, or nine mols of gas for every two equivalents of silver deposited. Therefore,

$$n_2 = W_s/2 \times \frac{107.88}{9} = \frac{W_s}{23.9733}\ .$$

In the final form the expression for vapor pressure reduces to

$$p = \frac{\frac{W_w}{18.016}}{\frac{W_w}{18.016} + \frac{W_s}{23.9733}} \times P.$$

For example, let us assume the data from the first experiment in Table I. Here, W_s = 16.5944 g. Ag, W_w = 0.41325 g. water, and P = 740.43 mm. The value of p, the vapor pressure of water at 25°, is found to be 23.7496 mm.

The simplicity of this method of calculating vapor pressures is apparent. *It is only necessary* to know three experimental values,—the corrected barometric pressure, and the weight, W_w, of water collected in the absorber while W_s grams of silver are being deposited in the coulometer. This indirect method of measuring the volume of gas passed through the liquid is unquestionably more accurate than any method used heretofore. Furthermore, the simple mol fraction equation, p = xP, used in the calculation does away with the complicated equations, and their many uncertain constants, required in other dynamic methods. The only point about which a question may be raised is the assumption of the validity of Dalton's law. In a sense, this method reduces vapor pressures to the same basis as that used in calculating atomic weights, viz., Ag = 107.88.

Application of the Method to Aqueous Solutions

As a test of the accuracy and duplication attainable we have applied the method to the measurement of the vapor pressures of pure water and aqueous solutions of potassium chloride and mannite. The results are collected in Tables I-IV. These are self-explanatory.

TABLE I

Vapor Pressure of Water at 25°

W_s Ag g.	W_w H_2O g.	n_2 H_2+O_2 mols.	n_1 H_2O mols.	n_1+n_2 Total mols.	P (corr.) mm.	p Vapor mm.
16.5944	0.41326	0.69220	0.02294	0.71514	740.43	23.749
14.2969	0.35760	0.59636	0.01985	0.61621	737.48	23.756
15.6673	0.39485	0.65353	0.02192	0.67545	731.87	23.747
15.0538	0.37212	0.62794	0.02065	0.64859	745.92	23.754
16.8377	0.42192	0.70255	0.02342	0.72577	735.86	23.745
14.6417	0.36258	0.61075	0.02012	0.63087	744.68	23.756
18.2425	0.45635	0.76095	0.02533	0.78628	737.37	23.754
16.9104	0.42010	0.70538	0.02332	0.72870	742.23	23.751
					Mean	23.752

The results thus obtained for water vapor show better agreement among themselves than those generally obtained by dynamic methods, heretofore. In only one case is the deviation from the mean as great as 0.007 mm. Also, the mean value, 23.752 mm., is identically the same as that obtained by Derby, Daniels and Gutsche[1], and it agrees favorably with the other values for the vapor pressure of water found in the literature. The following values have been obtained by other investigators at 25°.

[1] Derby, Daniels and Gutsche: J. Am. Chem. Soc., **38**, 793 (1914).

TABLE II

Vapor Pressure of Aqueous Solutions of Potassium Chloride at 25°.

M.	W_s Ag g.	W_w H_2O g.	n_2 H_2+O_2 mol	n_1 H_2O mol	P corr. mm.	p mm.	p mean mm.	p_o-p mm.	$\frac{p_o-p}{M}$
0.20	17.7227	0.44080	0.73926	0.02446	736.45	23.593			
	16.4055	0.40800	0.68432	0.02265	736.37	23.588			
	18.4370	0.45800	0.76906	0.02542	737.88	23.611	23.597	0.155	0.775
0.40	21.3610	0.52467	0.89103	0.02912	740.82	23.447			
	20.9742	0.51767	0.87489	0.02873	737.49	23.451			
	14.1376	0.34583	0.58972	0.01919	743.68	23.445	23.448	0.304	0.760
0.60	16.7350	0.40886	0.69806	0.02269	740.07	23.302			
	14.6971	0.35770	0.61306	0.01985	742.40	23.289			
	15.5702	0.37712	0.64948	0.02096	745.04	23.298	23.296	0.456	0.760
0.80	13.9353	0.34218	0.58128	0.01899	732.89	23.189			
	14.4390	0.35260	0.60229	0.01957	734.65	23.121			
	13.7586	0.33048	0.57391	0.01834	746.66	23.126			
	12.3099	0.29698	0.51348	0.01648	743.63	23.130			
	16.8350	0.41001	0.70224	0.02276	738.38	23.178			
	16.2922	0.39643	0.67959	0.02200	737.32	23.125			
	18.7112	0.44995	0.78050	0.02497	747.67	23.182			
	17.5324	0.42158	0.73133	0.02340	747.98	23.191	23.15	0.597	0.745
1.00	17.5576	0.42222	0.73238	0.02343	742.96	23.037			
	16.9542	0.40991	0.70721	0.02269	739.16	22.985			
	14.9746	0.36141	0.62463	0.02006	740.09	23.029	23.017	0.735	0.735

TABLE II (continued)

1.50	17.0601	0.40410	0.71163	0.02243	750.54	22.628			
	15.9783	0.37561	0.66650	0.02084	745.58	22.615			
	16.3163	0.38703	0.68060	0.02148	739.13	22.616	22.620	1.132	0.755
2.00	13.7540	0.31966	0.57372	0.01772	741.25	22.237			
	13.0884	0.30403	0.54595	0.01687	741.79	22.241			
	14.5530	0.33866	0.60704	0.01879	740.78	22.250	22.243	1.509	0.754
2.50	21.5220	0.49205	0.89774	0.02731	741.60	21.895			
	13.8685	0.31919	0.57849	0.01772	736.52	21.886			
	13.9650	0.32343	0.58252	0.01795	730.86	21.851	21.877	1.875	0.750
3.00	12.9575	0.29563	0.54049	0.01641	728.77	21.473			
	14.9132	0.33816	0.62207	0.01877	734.07	21.501			
	20.2510	0.45407	0.84473	0.02520	742.72	21.518	21.497	2.255	0.751
3.50	17.2996	0.37800	0.72162	0.02098	747.07	21.108			
	15.9324	0.34842	0.66549	0.01934	745.85	21.090			
	18.7850	0.41392	0.78358	0.02297	739.79	21.068	21.089	2.663	0.761
4.00	19.8143	0.42702	0.82651	0.02370	743.47	20.726			
	18.5494	0.39892	0.77375	0.02214	743.33	20.680			
	18.6468	0.40143	0.77781	0.02228	743.77	20.713			
	20.4302	0.43877	0.85220	0.02435	743.70	20.663	20.696	3.056	0.764
4.81	18.6775	0.38852	0.77909	0.02156	742.27	19.993			
	15.6524	0.32656	0.65291	0.01813	742.12	20.047			
sat'd.	18.0159	0.67470	0.75149	0.02080	742.33	19.991			
	12.0848	0.25118	0.50409	0.01394	745.05	20.052	20.021	3.731	0.776

Observer	Method	p_{25}
Regnault[1]	Dynamic	23.55 mm.
Lincoln and Klein[2]	Dynamic	23.76
Holborn and Henning[3]	Static	23.69
Eckholm[4]	Interpolation formula	23.79
Scheel and Heuse[5]	Static	23.76
Krauskopf[6]	Dynamic	23.71
Derby and Daniels[7]	Dynamic	23.75
Pearce and Snow	Dynamic	23.752

The complete data for the vapor pressures of aqueous solutions of potassium chloride are given in Table II. In this we have included all of the data obtained for each concentration of the salt, and we have simply taken the mean values without rejecting those values which appear to be in error. In some cases the agreement between the values for any one concentration is less than one might desire, and less, also, than the accuracy of which the method is capable. The vapor pressure values for the various solutions, however, are in general more consistent than those obtained by other modifications of the dynamic method. Most of the data presented was obtained during the extreme heat of the summer session. The deviations observed are due almost entirely to difficulties in controlling the temperature conditions accurately over a period of several hours. Under ideal conditions there is no reason why the accuracy obtainable should not approach that of the silver coulometer itself.

The values for the molal lowering of the vapor pressure are given in the last column. While they show considerable irregularity, they show also the same general trend as those calculated by Fraser, Lovelace and Sease[8], using their very accurate differential method. They have found that the curve for the plot of the molecular lowering of the vapor pressure, $(p_o - p)/m$, against the molar concentration passes through a distinct minimum at about 1.0 m, with a slight irregular hump in the curve between 0.4 m and 0.8 m. A rough plot of similar data obtained by our apparatus also shows a minimum in the molal lowering of the vapor pressure at 1.0 M, but the hump has its maximum in the neighborhood of 1.5 M. While there is undoubtedly a minimum value, the average value for the molal lowering for the twelve concentrations studied is 0.7572 mm. At no concentration does the deviation from this value exceed ± 0.02 mm., a value which could easily be accounted for by an error of 0.02 mm. to 0.03 mm. in the vapor pressure reading.

To test the efficiency of the apparatus further we have measured the vapor pressures of four aqueous solutions of mannite. The results obtained are given in Table III.

[1] Regnault: Ann. Chim. Phys., (3) **15**, 129 (1845).
[2] Lincoln and Klein: J. Phys. Chem., **11**, 318 (1907).
[3] Holborn and Hoenning: Ann. Physik, (4) **26**, 833 (1908).
[4] Eckholm: Arkiv. Math. Astr. Phys., **4**, 29 (1908).
[5] Scheel and Heuse: Ann. Physik, (4) **31**, 715 (1910).
[6] Krauskopf: J. Phys. Chem., **14**, 489 (1910).
[7] Derby and Daniels: J. Am. Chem. Soc., **38**, 793 (1914).
[8] Fraser, Lovelace and Sease: J. Am. Chem. Soc., **43**, 106 (1921).

TABLE III

Vapor Pressures of Mannite Solutions at 25°

M	W_s Ag g.	W_w H_2O g.	n_2 H_2+O_2	n_1 H_2O	P corr. mm.	p mm.	p mean mm.
0.4	27.9611	0.69045	1.16634	0.03832	741.53	23.590	
	18.5629	0.45535	0.77431	0.02527	745.95	23.579	
	21.4427	0.52757	0.89444	0.02928	744.08	23.588	23.586
0.6	18.9621	0.46340	0.79096	0.02572	745.80	23.489	
	16.5346	0.40452	0.68971	0.02245	745.44	23.503	
	16.0165	0.39180	0.66809	0.02175	744.64	23.475	
	18.7486	0.45880	0.78206	0.02546	746.10	23.529	
	18.3812	0.45037	0.76673	0.02499	744.48	23.506	
	15.8026	0.38792	0.65917	0.02153	742.76	23.495	23.499
0.8	18.5624	0.45638	0.77429	0.02533	738.83	23.406	
	15.9094	0.39143	0.66363	0.02173	738.99	23.427	
	18.5963	0.45709	0.77571	0.02537	739.20	23.412	23.415
1.0	13.7688	0.33604	0.57434	0.01865	741.92	23.337	
	17.3198	0.41907	0.71830	0.02326	743.41	23.319	
	20.0870	0.49080	0.83789	0.02724	740.82	23.328	23.326

The values for the vapor pressure of the solvent for the two series of solutions are graphically shown in Fig. 2. The extreme smoothness of the curves and the fact that the points fall so nearly upon a straight line speak for the accuracy obtainable by the method. The curve for mannite is a straight line throughout. For potassium chloride solutions up to 3.5 M the maximum displacement from the straight line curve does not exceed 0.02 mm., and at 4.8 M the deviation is only 0.10 mm. The striking apparent proportionality between the vapor pressure lowering, $p_o - p$, and the molality for solutions of potassium chloride up to 0.6 M is shown in Fig. 3. Within limits of experimental error the curve for mannite solutions is a straight line, as we should expect.

TABLE IV

Observed and Calculated Vapor Pressure Lowering produced by Mannite at 25°

M	X mol fract.	P mm.	$p_o - p$ obs. mm.	$p_o - p$ calc. mm.	$\frac{p_o - p}{M}$ mm.
0.0	0.000000	23.752	0.000	0.000	
0.4	0.007155	23.586	0.166	0.169	0.415
0.6	0.010694	23.499	0.252	0.254	0.420
0.8	0.014208	23.415	0.337	0.3375	0.421
1.0	0.017697	23.328	0.424	0.420	0.420

According to Raoult's law the lowering of the vapor pressure of a solvent is directly proportional to the mol fraction, x, of the solute. For comparison, the observed values for $p_o - p$ for mannite solutions and those calculated from Raoult's law are given in Table IV. The last column contains the calculated values for the molal lowering of the vapor pressure produced by mannite. In both cases the agreement is satisfactory.

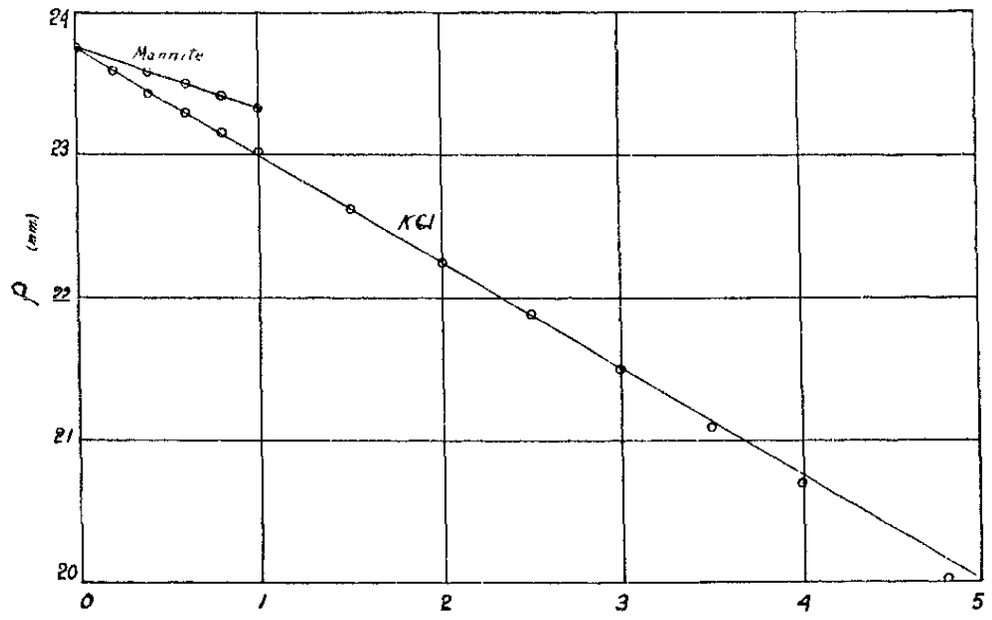


FIG. 2

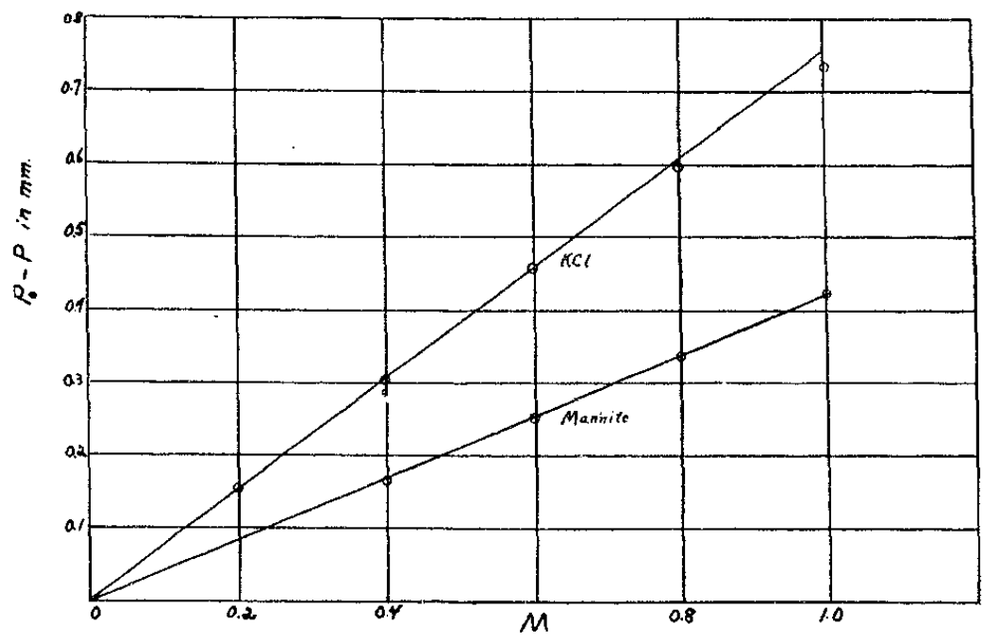


FIG. 3

Summary

1. A new modification of the dynamic method of measuring vapor pressures has been developed.

2. The method introduces the following new features. Instead of measuring the volume of air which passes through the solution, hydrogen and oxygen are generated electrolytically, and the volume of the mixed gases, as well as the number of mols of each, is calculated from the weight of silver deposited in a coulometer.

3. The actual calculation of the vapor pressure requires the knowledge of three single values, viz., the corrected barometric pressure, P, and the weight of the vapor, W_w, taken up by the absorber while W_s grams of silver are being deposited in the coulometer. The number of mols of water vapor, n_1, and the total number of mols of hydrogen and oxygen, n_2 are calculated from W_w and W_s, respectively. From this data the vapor pressure of the solvent is calculated by means of the simple equation,

$$p = \frac{n_1}{n_1 + n_2} P.$$

4. The method has been applied to the determination of the vapor pressures of pure water and aqueous solutions of potassium chloride and mannite at 25°*.

Physical Chemistry Laboratory,
The State University of Iowa.

* The method is being extended to the determination of the vapor pressure of aqueous solutions up to the limits of solubility.

THE METHANE EQUILIBRIUM. III

BY R. C. CANTELO

A. The Catalytic Decomposition of Ethylene

(1) The Materials used:

Ethylene—The ethylene was prepared by the action of phosphoric acid upon absolute alcohol. The gas so prepared analyzed 96-98% C_2H_4.

(2) Contact Materials:

Of the various contact agents used, nickel reduced from the oxide was the only efficient one. It alone will be considered here. The catalytic nickel was prepared according to the method described in the first paper of this series.

(3) The Apparatus:

This consisted of a "train" similar to that described in the previous paper. The reaction chamber was a Pyrex glass tube which was heated in a specially constructed gas oven. The temperature of the tube was taken by two thermometers placed in contact with the glass tube; and the temperature of the oven could be controlled easily to 5 degrees.

(4) Experimental Method:

In the first series of experiments the gas was passed but once over the catalyst; but in those experiments designed to test the stability of ethane at 360°C, the gaseous products were passed backwards and forwards over the catalyst a varying number of times at the rate of one to two liters per hour. Hydrogen was used for the preliminary washing-out of the apparatus.

The gaseous products were collected in every case over a 1:1 mixture of glycerol and water.

(5) Method of Analysis:

Carbon dioxide, unsaturated hydrocarbons, oxygen and carbon monoxide were determined by the usual absorption methods.

Hydrogen was determined by combustion at 270-300°C with copper oxide in a small quartz tube, heated in a small gas oven the temperature of which could be controlled easily. To assist the rate of combustion of hydrogen, some metallic copper was always present at the start of the combustion.[1] The reduction in volume after combustion was equivalent to the c.c. of hydrogen in the gas.

It was found, however, that when the percentage of hydrogen in the gas was small, there was some loss due to the combustion of some ethane. This was overcome by adding 15 to 20 c.c. of pure electrolytic hydrogen. Tests then showed the method to be satisfactory. The temperature for rapid and complete combustion of hydrogen alone varied slightly with the quartz tube used. For the tube finally used in this series, the average temperature was 280°C.

[1] Pease and Taylor: J. Am. Chem. Soc., **34**, 2179 (1921).

Methane and ethane were determined in the residue from the combustion of the hydrogen. The quartz tube was heated directly by a free flame some 3 inches wide, and the temperature was that of a bright red heat.

From the equations:

$$4\ CuO\ (s) + CH_4\ (g) \rightleftarrows CO_2\ (g) + 2\ H_2O\ (l) + 4\ Cu\ (s)$$
$$x\ c.c. \qquad x\ c.c.$$
$$7\ CuO\ (s) + C_2H_6\ (g) \rightleftarrows 2\ CO_2\ (g) + 3\ H_2O\ (l) + 7\ Cu\ (s)$$
$$y\ c.c. \qquad 2\ y\ c.c.$$

it follows that the increase in volume after combustion equals y c.c. = c.c. of C_2H_6 and again

$x + 2\ y$ = c.c. of CO_2 from which x is easily determined.

(6) Experimental Results:

Experiments were carried out at temperatures from 150 to 350°C. The results given in Table I are those for 300 to 350°C only. The analyses have been calculated to nitrogen free.

TABLE I

Catalyst—reduced nickel oxide

	Analyses of products						
Temperature	CO_2	C_2H_4	O_2	CO	CH_4	C_2H_6	H_2
300	0.6	1.6	0.0	1.3	32.9	47.0	16.6
325	0.8	18.4	0.0	0.8	33.1	29.9	17.0
325	0.4	5.9	0.4	0.8	30.5	40.4	21.6
325	0.4	6.0	0.4	0.9	30.5	40.4	21.4
350	0.0	0.9	0.0	1.3	42.3	34.1	21.4
350	0.9	0.0	1.7	0.0	40.2	36.7	20.5

From Table I, it is evident that above 300°C, methane is formed in addition to ethane by the catalytic decomposition of ethylene. Ethane, however, appears to be stable even up to 350°C; and this is in direct contradiction with Sabatier's statement that with a sufficiently long tube or a sufficiently slow rate ethylene might be decomposed completely into methane, hydrogen and carbon.[1] It was necessary to test the validity of this view as it conflicts with the theoretical conclusions drawn by the writer.

The following experiments establish the stability of ethane up to 360°C in the presence of nickel catalyst.

Ethylene analyzing 95% C_2H_4 was passed back and forth from one gasometer to another over a nickel catalyst heated to 360°C.

The data obtained were as follows:—

Volume of C_2H_4 used—2300 c.c.
Rate—about one liter per hour.
Total time gas circulated—5 hrs. 15 min.
Volume of resulting gas—1800 c.c.

[1] Sabatier: Compt. rend., **124**, 616, 1359 (1897); **131**, 267 (1900).

The experiment was continued on the following day.

Final volume of resulting gas—1800 c.c.

Total additional time gas circulated—3 hrs. 15 min.

Total time—8.5 hrs.

Analysis of final product
(Calculated to nitrogen—free)

CO_2	C_2H_4	O_2	CO	CH_4	C_2H_6	H_2
0.0	0.0	0.0	0.7	68.2	25.2	5.6

It would be useless, therefore, to attempt to determine the equilibrium constant for the methane, carbon, hydrogen system at or below 360°C, when ethylene is used as the initial system.

B. Methane Equilibrium with Ethylene as the Initial System

The apparatus used was the same as that described in the first paper of the series. The ethylene was prepared in the usual way from absolute alcohol by the dehydrating action of phosphoric acid. The experimental method, however, was varied slightly, in that at the end of an experiment, before the next one was started one-half of the nickel catalyst was removed and replaced by freshly prepared material. It was hoped that in this way, the life of the catalyst would be lengthened. The method of analysis was varied slightly. After a preliminary analysis to determine the absence of ethane, the analysis was repeated using the direct combustion method for the determination of methane and hydrogen.

Preliminary experiments showed that the successive analyses of the product differed after each passage over the catalyst until a point was reached where the analyses remained constant, i. e. until the equilibrium point was reached. This was found to correspond fairly well with the point where further passages produced no further increase in volume. Accordingly the gaseous products were circulated until the change in volume became zero, and were then circulated for two to three hours in addition.

It seemed probable that continued circulation of the gas would lead to lower values for Kp than those calculated upon the basis of amorphous carbon alone. It is inevitable that some graphitization of the carbon will occur when it is subjected to a high temperature over a long period of time. In the actual equilibrium experiments, every attempt was made to reproduce as nearly as possible the same system in the duplicate experiments.

The experimental results follow in Table II.

Table III is a summary, in which the writer's values (C) are compared with the average values of Mayer and Altmayer[1] (M & A). The initial system is specified in each case. To complete the table, calculated values are given (Saunders' Equation for amorphous carbon),[2] as are also the determined values of Coward and Wilson[3] (C & W) for temperatures above 800°C.

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[1] Ber., **40**, 2134 (1907).

[2] J. Phys. Chem., **28**, 1151 (1924).

[3] J. Chem. Soc., **115**, 1380 (1919).

TABLE II

Temperature °C.	Analyses CO_2	O_2	CO	CH_4	H_2	$\frac{P_{CH_4}}{P^2_{H_2}}$ K_P	(Calc.)
510	0.0	0.0	2.6	50.4	38.5	3.4	3.9
510	1.0	0.0	2.1	55.8	34.6	4.6	3.9
565	0.9	0.0	1.8	36.1	57.7	1.1	1.3
615	0.0	0.0	1.5	22.6	72.2	0.43	0.67
615	0.0	0.0	0.0	20.3	77.1	0.34	0.67
670	0.0	0.0	1.2	12.6	81.5	0.19	0.35
670	0.0	0.0	0.9	12.3	82.7	0.18	0.35

TABLE III

Temperature °C.	KP, Calc'd.	M & A Average	C	C & W	Initial System
508		3.6			CH_4
506		1.8			C + H
510	3.9		3.4		C_2H_4
510	3.9		4.6		C_2H_4
536		2.8			CH_4
536		1.7			C + H
565	1.3		1.1		C_2H_4
565	1.3		0.95		CH_4
567		1.9			CH_4
567		1.3			C + H
577		0.78			C + H
607		0.57			C + H
615	0.67		0.43		C_2H_4
615	0.67		0.34		C_2H_4
625		0.34			C + H
670	0.35		0.43(?)		CH_4
670	0.35		0.51(?)		CH_4
670	0.35		0.19		C_2H_4
670	0.35		0.18		C_2H_4
770	0.12		0.12		CH_4
850	0.05			0.025	CH_4
1000	0.02			0.015	C + H
1000	0.02			0.011	CH_4
1100	0.01			0.006	CH_4
1100	0.01			0.006	C + H

Table III shows that the results of Mayer and Altmayer are of the same order as those determined by the writer. In addition it shows that the determined results are as a rule lower than the calculated.

The results obtained with ethylene as the initial system probably represent the equilibrium between amorphous carbon, methane and hydrogen more

closely than any of the other values. These results are strictly comparative. In each of these experiments fresh catalyst was used; and the carbon was the amorphous material precipitated by the thermal decomposition of ethylene. It must be admitted, however, that some graphitization of this material would take place over the long period during which the gases were circulated.

Summary

The catalytic decomposition of ethylene was studied and it was found that the special nickel-nickel oxide catalyst was most effective in bringing about this decomposition. At 300°C and higher temperatures, methane is found in the gaseous decomposition products, the percentage of methane following one passage of the gas over the catalyst, increasing with the temperature.

Experiments in which the gaseous products were passed repeatedly over the catalyst proved that ethane was stable in the presence of a nickel catalyst up to 360° C.

Experiments in which the gaseous products of the catalytic decomposition of ethylene (at 500°C and above) were circulated repeatedly over a nickel-nickel oxide catalyst showed that the methane equilibrium should be attained in this manner.

Equilibrium constants for the methane equilibrium at 500 to 770°C were obtained by repeatedly circulating the products of the catalytic decomposition of ethylene over the nickel catalyst. These constants are in general agreement with those obtained by other investigators.

Department of Chemistry,
University of Cincinnati,
Cincinnati, Ohio.

1-60

ADSORPTION EQUATIONS
A REVIEW OF THE LITERATURE

BY ENOCH SWAN AND ALEXANDER ROBERT URQUHART

Contents

INTRODUCTION.

Nomenclature: Evaluation of the Quantities; Classification.

I. THE GENERAL ADSORPTION EQUATION.

Empirical: Freundlich; Müller.

Theoretical: Gibbs, and related equations of Harkins, Thompson, Warburg, Lewis, Porter, and Polanyi; Langmuir; Frenkel; Volmer; Henry; Eucken; Lorentz and Lande; Polanyi; Iliin.

II. THE ISOTHERM.

Empirical: The "exponential" equation, and related equations of Schmidt and Hinteler, and McGavack and Patrick; Gurwitsch; Freundlich's equations; Rakovski; Kayser; Schmidt; Homfray; Trouton.

Theoretical: Deductions of the "exponential" equation by Robertson, Kolthoff, and Henry; Ostwald and Izaguirre; Gurwitsch; Stadnikoff; Pavlov; Reichinstein; Duhem; Schmidt's first equation; Arrhenius; Schmidt's second equation; Williams; Henry; Gorbatschew.

III. THE ISOBAR.

Empirical: Kayser; Ostwald; Freundlich.

Theoretical: Williams; Iliin.

IV. THE ISOSTERE.

Empirical: Freundlich; Homfray

Theoretical: Williams; Henry.

V. RATE OF ADSORPTION.

Empirical: Mills and Thomson; Bergter; Lagergren; Pickles; Burt and Bangham; Zacharias; Freundlich; Dietl; Davis and Eyre; Fisher.

Theoretical: McBain; Marc; Gustaver; Henry; Iliin.

VI. HEAT OF ADSORPTION.

Empirical: Freundlich; Homfray; Lamb and Coolidge; Katz and Hollemman.

Theoretical: Williams; Eucken; Lorentz and Lande; Polanyi: Harkins; Iliin; Tarasoff.

CONCLUSION.

Note on the Formulation of Adsorption Laws.

Introduction

The great importance of the part played by adsorption phenomena in natural processes is now well recognised, and in consequence of this recognition a large amount of work has been done with a view to discovering the laws which underlie such phenomena, and more particularly to make these laws more concise and readily understandable by expressing them in mathematical form. As a result of this work many adsorption equations are extant, and though none is completely satisfactory, most are valuable as approximations to the truth in a more or less restricted region. In the present paper an attempt has been made to collect in one place the various equations that have been proposed, and to consider in how far they are applicable to actual adsorption systems.

In its strictest sense the word adsorption designates the concentration of one phase at its interface with another, but the filling of pores in the adsorbent, which may accompany true adsorption, is occasionally included in a looser use of the term. In this paper these capillary effects will be considered adsorption just as far as the authors concerned have so considered them, but the adsorption of a gas by a liquid and of a liquid by a liquid will not be discussed.

Nomenclature.

As it is desirable to retain one set of symbols in order to avoid the frequent repetition of definitions, the following will as far as possible be used throughout, irrespective of the actual symbols used by the various authors in the original papers.

Let

m = mass of adsorbent.
v = volume of medium surrounding adsorbent.
X = mass of adsorbate adsorbed by *m* grams adsorbent.
x = mass of adsorbate adsorbed by 1 gram adsorbent.
s = mass of adsorbate adsorbed by 1 gram adsorbent at saturation.
p = equilibrium pressure of adsorbed gas or vapour.
P = saturation pressure of adsorbed gas or vapour.
c_o = initial concentration of solution.
c = equilibrium concentration of solution.
θ = temperature Centigrade.
T = temperature Absolute.
t = time.
H = total heat of adsorption.
R = gas constant.
n, k_1 k_2, etc., constants.

Evaluation of the Quantities.

The experimental determination of most of the above quantities presents no great difficulty, but the evaluation of the amount adsorbed, x, has not always been accurately performed. When adsorption is from the gaseous phase a knowledge of the total volume of the system and the initial and equilibrium

pressures is sufficient to determine x. It seems hardly necessary to add that account should be taken of the volume of the adsorbent, yet this has sometimes been neglected. This method of determining x neglects the volume of the adsorbed gas, but this error is usually quite unimportant.

In the majority of investigations of adsorption from solution x has been taken as equal to $(c_o - c)w$ or $(c_o - c)v$, where c denotes the concentration in grams per unit weight or volume, and w and v are respectively the original weight and volume of solution. Williams,[107] however, has pointed out that this calculation of x assumes that the mass or volume of the solvent remains constant during adsorption, and that no solvent is adsorbed. Neither of these assumptions is justifiable, though the error introduced by the former is sufficiently small to be neglected when the solution is very dilute. Williams has further shown that if M is the mass of solution, and concentrations are expressed in grams solute per gram solution, then

$$x_o = \frac{M}{m} \cdot \frac{c_o - c}{1 - c},$$

where x_o is the amount adsorbed calculated on the assumption that no solvent is adsorbed. If x and y represent the true adsorption values of solute and solvent respectively, then

$$x = x_o + y \frac{c}{1 - c}.$$

In general x and y cannot be determined, but Williams has given two empirical equations from which approximate values may be deduced. This analysis, which leads to a simple explanation of negative adsorption,[109] has more recently been substantiated by Gustafson.[32]

It is of interest to note that Mecklenburg[68] has recently proposed a graphical method for the determination of the equilibrium concentration when the amount adsorbed is known.

Classification.

For convenience the problems to be solved may be regarded as the formulation of the following six functions:

1. The General Adsorption Equation, $x = \varphi(c, T)$.
2. The Isotherm, $x = \varphi(c)$.
3. The Isobar, $x = \varphi(T)$.
4. The Isostere, $c = \varphi(T)$.
5. Rate of Adsorption, $x = \varphi(t)$.
6. Heat of Adsorption, $H = \varphi(x)$.

I. The General Adsorption Equation

Empirical.

Freundlich[22] has developed a method for the representation of adsorption from solution at any concentration and temperature, depending on the use of the equations

$$\log \lambda_t = \log \lambda_o - k_1 \left(\log \frac{a}{v} \right)^{\theta}$$

and $$\left(\frac{a}{v}\right)_\theta = \left(\frac{a}{v}\right)_\circ - S^\theta$$

in combination with his λ equation. (q. v. section II.)

Müller[72] found that the absorption of water vapour by textile fibres could be expressed by the equation

$$x = (k_1 + k_2\, p/P)\sqrt{100 - \theta}$$

This equation is valueless except perhaps over a very limited pressure and temperature range, both the assumptions involved in it—that of a linear relationship between x and p/P and that of zero adsorption at the boiling point—being quite unsound.

Theoretical.

The earliest theoretically derived equation is that deduced by Gibbs.[29] In 1874 Gibbs showed thermodynamically that if Γ is the surface excess, σ the surface tension, and μ the chemical potential of the adsorbed substance in solution, then

$$\Gamma = -\frac{d\sigma}{d\mu}$$

Writing $\mu = RT\log(A + k)$ where A is the activity of the solute then

$$d\mu = RT\ d\log A$$

and $$\Gamma = -\frac{d\sigma}{RT\ d\log A}$$

For very dilute solutions $A = c$, and hence $\Gamma = -\frac{c}{RT}\frac{d\sigma}{dc}$.

which is the usual form of the Gibbs equation.

This equation is usually interpreted qualitatively as meaning that if a dissolved substance lowers the surface tension at an interface then it will be positively adsorbed at that interface. Bancroft[3] has shown that this interpretation is not a logical conclusion for the interface solid-liquid. Wo. Ostwald[74] extends the usual interpretation of the equation as follows: "Adsorption will take place whenever there exists at a surface a difference in energy potential which can be decreased by a change in the concentration of the dispersed material bordering the surface."

Amongst other authors who have published proofs of the Gibbs equation are Milner,[71] Harlow and Willows,[37] Williams,[111] Iredale,[44] and W. Ostwald.[73]

A deduction of the equation has also been given by Harkins,[35] who has shown that

$$\Gamma = -\frac{c}{RT}\frac{d\sigma}{dc} = -\frac{c'}{RT}\frac{d\sigma}{dc'}$$

where c' is the concentration of the solute in the vapour.

Thompson[103] in 1888 deduced the relationship

$$c + \Gamma = ce^{-\frac{1}{RT}\frac{d\sigma}{dc}}$$

which yields the usual Gibbs form on expanding and neglecting higher terms.

That the surface layer cannot be homogeneous with the remainder of the liquid was shown by Warburg,[106] who for sodium chloride solutions obtained a relation for the surface deficit similar to that of Gibbs.

Lewis,[58] using a somewhat simpler method than Gibbs, has found the equation of electrocapillary adsorption to be

$$\Gamma_{\text{salt}} + \Gamma_{\text{cation}} + \Gamma_{\text{anion}} = -\left[\frac{c}{RT}\frac{d\sigma}{dc} + (a+b)\frac{d\sigma}{d\pi}\right]$$

where a and b are the electrochemical equivalents of anion and cation, and π is the potential difference at the interface. A slight error in Lewis' original proof has been pointed out by Partington.[76]

Porter[87] is the only author who has derived the equation for concentrated solutions. He finds that

$$\Gamma = -\frac{(1-ac)^2 c}{RT}\frac{d\sigma}{dc}$$

where c is the ratio of solute molecules to solvent molecules (n/N), and a is Callendar's hydration factor, obtained from the equation

$$\log (P/p) = \frac{n}{N - an}$$

It is of interest to note that Polanyi[79,80] has shown that for a swelling gel

$$\Gamma = \frac{c}{RT}\frac{d\pi}{dc}$$

where π is the swelling pressure. In a later paper[86] some results of Loeb have been used to provide experimental confirmation of this equation.

Freundlich[28] considers the Gibbs equation to be of limited application, and has stated that the more general equation would be

$$\Gamma = -f(c, T)\frac{d\sigma}{dc}$$

in which all that is known about f(c,T) is that it is positive. The usual form of the equation is obtained by assuming the van't Hoff Laws, and hence is limited with these laws to dilute solutions. Even for dilute solutions, however, Freundlich is doubtful of the soundness of the deduction, since the surface tension depends on factors, such as solvation, which are not considered in the van't Hoff laws. Langmuir,[56] on the other hand, believes that the deduction is sound for dilute solutions, since the gas laws in some of the derivations,—for example Milner's—are applied only to the interior of the solution. It should be noted, however, that the equation is definitely limited to true solutions, and cannot be applied to colloidal solutions, a point which has been emphasized by Bancroft.[3] All the deductions of the equation assume the thermodynamic reversibility of the adsorption process, the validity of which assumption may in some instances be in slight doubt.

Many attempts have been made to obtain confirmation of the equation, but the great experimental difficulties have prevented any definite conclusion being reached. Donnan has recently said "the question whether the simplified form of the Gibbs equation yields a sufficiently accurate value for the excess surface concentration can scarcely be decided without further experimental evidence."

According to Langmuir's[54] theory of adsorption the adsorbate is held by the unsatisfied secondary valences of the adsorbent to form a continuation of the space lattice of the latter, so that the adsorbent forms a true chemical compound with the adsorbate. It is assumed that all molecules striking a surface condense, and that evaporation takes place subsequently, so that adsorption is the equilibrium condition representing the time-lag of condensation over evaporation. Since the force of attraction is much less at the second layer than at the first, molecules will evaporate much more quickly from the second layer, and hence it is to be expected that a monomolecular layer will be exceeded only at high pressures or concentrations. Langmuir's theory is derived specifically for true adsorption at a plane surface, and neglects capillary effects.

A consideration of the dynamic equilibrium between rate of evaporation and rate of condensation leads to a number of equations according to the conditions obtaining at the surface.[55,57]

(1) The plane surface has only one kind of space lattice.

Then
$$\theta = \frac{k\mu}{\nu + k\mu} = \frac{N}{N_o}\eta$$

where θ is the fraction of the surface covered

ν is the rate at which the gas would condense if the surface were completely covered

μ is the number of moles of the gas striking each square centimetre per second. From the kinetic theory $\mu = \frac{\rho}{\sqrt{2\pi MRT}}$

N is Avogadro's Constant

N_o is the number of elementary spaces per square centimetre

η is the number of moles of gas adsorbed per square centimetre

Under these conditions adsorption should be large and nearly independent of pressure at low temperatures, while at higher temperatures adsorption should be small and proportional to pressure.

(2) The plane surface contains more than one kind of elementary space.

Then
$$\frac{N}{N_o}\eta = \Sigma\beta_1\theta = \Sigma\frac{\beta_1 k\mu}{1 + k\mu}$$

where β_1, β_2, . . . etc., represent the fractions of the total number of elementary spaces occupied by each kind.

(3) Amorphous surfaces—all the elementary spaces may be unlike.

$$\frac{N}{N_o}\eta = \int_0^1 \frac{a\mu d\beta}{1 + a\mu}$$

where a is a function of β. In Langmuir's opinion this equation should be true for porous bodies.

(4) Each elementary space may hold more than one adsorbed molecule.

$$\frac{N}{N_o}\eta = \frac{k_1\mu + 2k_1k_2\mu^2 + 3k_1k_2k_3\mu^3 + \ldots}{1 + k_1\mu + k_1k_2\mu^2 + k_1k_2k_3\mu^3 + \ldots}$$

This equation may also be expected to hold when adjacent molecules influence each other's rate of evaporation.

(5) Atomic adsorption—the elementary spaces are occupied by individual atoms of the adsorbate.

$$\eta = \tfrac{1}{2}\sqrt{\frac{N_o}{N}k\mu}$$

If $\theta \longrightarrow 1$, i.e. adsorption is small,

$$\eta \propto \rho^{\frac{1}{2}}$$

(6) Adsorbed films more than one molecule thick

$$\frac{N}{N_o}\eta = \frac{k}{1/\mu + a + b\mu + c\mu^2 + \ldots}$$

where $a = k_1 - 2k_2$

$b = k_2(4k_2 - 3k_3 - k_1)$

$c = 2k_2(6k_2k_3 - 2k_3k_4 + k_1k_2 - k_1k_3 - 4k_2)$

This equation shows that at very low pressure η is proportional to μ, but at pressures close to saturation η begins to increase rapidly, and is infinite when saturation is reached.

Langmuir's equations have not yet received adequate experimental confirmation over large pressure ranges, which may perhaps be attributed to the difficulty of expressing the equations in terms of measurable quantities, and also to the fact that the conditions under which they may be expected to hold are ideal rather than readily attainable.

In adducing much evidence in favour of the existence of monomolecular films of oil on water from the experimental work of, amongst others, Milner, Syskovski, and Traube, Langmuir[56] has made use of a new relation between Γ and c, viz.,

$$\Gamma = c\,k\,e^{\frac{\lambda}{RT}}$$

where λ is the decrease in potential energy which occurs when one mole of solute passes from the interior of the solution into the surface layer.

A theory similar to that of Langmuir, has recently been put forward by Frenkel,[21] while equations of the same type have been obtained thermodynamically by Volmer.[105]

Henry[39] has developed equations based on the conceptions of surface energy introduced by Hardy and Langmuir. The fundamental assumptions are, first, that the range of action of adsorption forces is comparable with atomic diameters; second, that the impact of a molecule is completely inelastic. By applying to the kinetic equilibrium Jeans' equations for the rate of impact and Langmuir's equation for the rate of evaporation, general equations for the rate of adsorption, the isotherm and the isostere are developed for the adsorption of each of n gaseous components. Examples of these equations are given later.

According to Eucken,[17] there is around an adsorbent an "atmosphere" of adsorbed gas in a state of compression, the density of any layer of this atmosphere varying with its distance from the surface. It is assumed that the adsorbed molecules have no interaction, and that the relation between force (F) and distance (h) is

$$F = -\frac{k}{h^{\mu+1}}$$

where μ is a constant. In a manner similar to the derivation of the barometric height formula the equation representing the adsorption of a perfect gas by a plane surface of area O is obtained in the form

$$X = OC_\infty \int_\delta^\infty \left(e^{-\frac{Fh}{RT}} - 1 \right) dh$$

where δ is the mean molecular diameter, and C_∞ is the number of moles of gas in unit volume at a distance from the surface corresponding to zero attractive force. By evolving in series and integrating an approximate solution is obtained

$$X = \frac{O\delta\, C_\infty e^{\frac{k_2}{T}}}{\mu\frac{k_2}{T} - k_3}$$

Other equations are given for the adsorption of a perfect gas by a segmented surface, the adsorption of a real gas by a plane surface, and the adsorption of a vapour by a segmented surface. In a more recent paper Eucken[18] has rederived those equations making use of Boltzmann's relation between the potential energy of a single particle and its distance from the surface. Throughout this work it is assumed that $\mu = 3$, which is hardly in agreement with modern opinion.[16] Nevertheless, the theory is in good agreement with experimental data; the same value for k_2 is obtained whether it is calculated from (1) the temperature coefficient of gaseous viscosity, (2) van der Waals' theory or (3) the heat of adsorption.

Polanyi[85] has adversely criticised Eucken's theory, and has concluded that it is not applicable to any of the markedly curved isotherms.

Lorentz and Lande[59] believe that Debye's work on the dipolarity of molecules is opposed to the conception of a purely molecular force of adsorption, and they conclude in contradistinction to Eucken, that adsorption

potential should in general vary with temperature. For the temperature range in which x varies as p they deduce the equation

$$X = \frac{O\delta C_\infty \epsilon^{k/T}}{2\mu\left(\frac{k}{T}\right)^2},$$

which is very similar to that obtained by Eucken. It is also shown that the apparent independence of potential on temperature found by Eucken, cannot be adduced as evidence against the dipolar molecular theory.

Polanyi[81] by considering with relation to the Third Law the heat and free energy of wetting has deduced that at low temperatures an adsorption system behaves as an ideal concentrated solution, whilst with increasing temperature the behaviour gradually approaches that of a dilute solution. By assuming that the adsorbed layer is highly compressed by the molecular forces and that the "exponential" equation holds, he has concluded that the molecular force varies as the distance. (cf. Edser[16]).

In a later paper Polanyi,[82] still assuming a highly compressed layer more than one molecule thick, has shown how to calculate the adsorption at any temperature and pressure if one isotherm is known. As a result of the compression a vapour will exist in the adsorption layer in the liquid state; if it is assumed that the internal pressure of this liquid is identical with that of the liquid in bulk then from thermodynamics it follows that $\epsilon_x = RT \log P/p$ where ϵ_x is the adsorption potential at a distance i, corresponding to an amount x adsorbed. If now an isotherm is known for any temperature below the critical, the relation $\varphi_i = x/\delta_o$ where δ_o is the density of the compressed layer, assumed equal to that of the liquid, and φ_i is the volume of the adsorption space to a distance i from the surface, allows of the plotting of a curve showing the relation between ϵ and φ. It being assumed that this relation does not vary with the temperature, a curve can be drawn showing ϵ_i against δ_i, provided the equation of state of the adsorbed substance is known. This calculation of δ_i varies according as (1) the gas is condensible, (2) the gas is not so condensible (3) the gas is in the transition region between (1) and (2). Lastly a curve can now be drawn showing δ_i against φ_i, and mechanical integration of this curve gives the amount adsorbed, since

$$x' = \int_o^{\varphi_{max}} \delta \,.\, d\varphi - d_x \,.\, \varphi_{max}$$

where x' is the adsorption excess, d_x is the density of the free gas space, and φ_{max} is the volume of the total adsorption space.

According to this theory the adsorption excess isotherm is divisible into a first part where the ideal gas laws are applicable and x varies as p, a second part where the a/v^2 of van der Waals' equation predominates and the compressibility decreases more slowly than $1/p$, and a third part where van der Waals' b predominates and the compressibility decreases more quickly than $1/p$. The theory also indicates that the saturation value should vary with the temperature, and in a later paper Polanyi[85] claims superiority of his theory over that of Eucken on this account.

Calculations according to the theory are in excellent agreement with experimental data, and this agreement is regarded as proof of the validity of the assumption that the adsorption potential is independent of the temperature.[83] Assuming the electrical origin of attraction, Polanyi therefore concludes that the cause of cohesion is a deformation of the molecules to bring opposite charges as near as possible.

The theory has been extended to solutions[84] but there is not sufficient suitable experimental evidence to allow of the verification of this extension; qualitatively, however, it is in agreement with Freundlich's rule that substances which are strongly adsorbed from solution permit only of weak adsorption from solutions in which they act as solvents.

Berenyi[6,7] has developed two new methods of calculating the $\epsilon - \varphi$ diagram, one by the use of the pressure-density tables of Amagat, the other depending on the Nernst rule of corresponding states. The latter method can be applied only at temperatures between 6 and 1.4 times the boiling point, to substances whose boiling points lie between 170° and 400° A.

As stated before, Lorentz and Lande[59] disagree with the assumption of temperature independence of potential, but they have shown that Polanyi's theory is in agreement with the application of the theorem of corresponding states to adsorption in the $p - \theta$ region where Henry's Law holds but where the pressure is not greater than the critical pressure and the temperature not less than the critical temperature.

Polanyi's theory is well supported by the experimental data tested, yet it is based on three unproved assumptions; (1) It is assumed that the potential ϵ and with it van der Waals' a is independent of the temperature. (2) It is assumed that the potential is independent of whether the remaining space is empty or not. (3) It is assumed that the equation of state is applicable to an adsorbed gas.

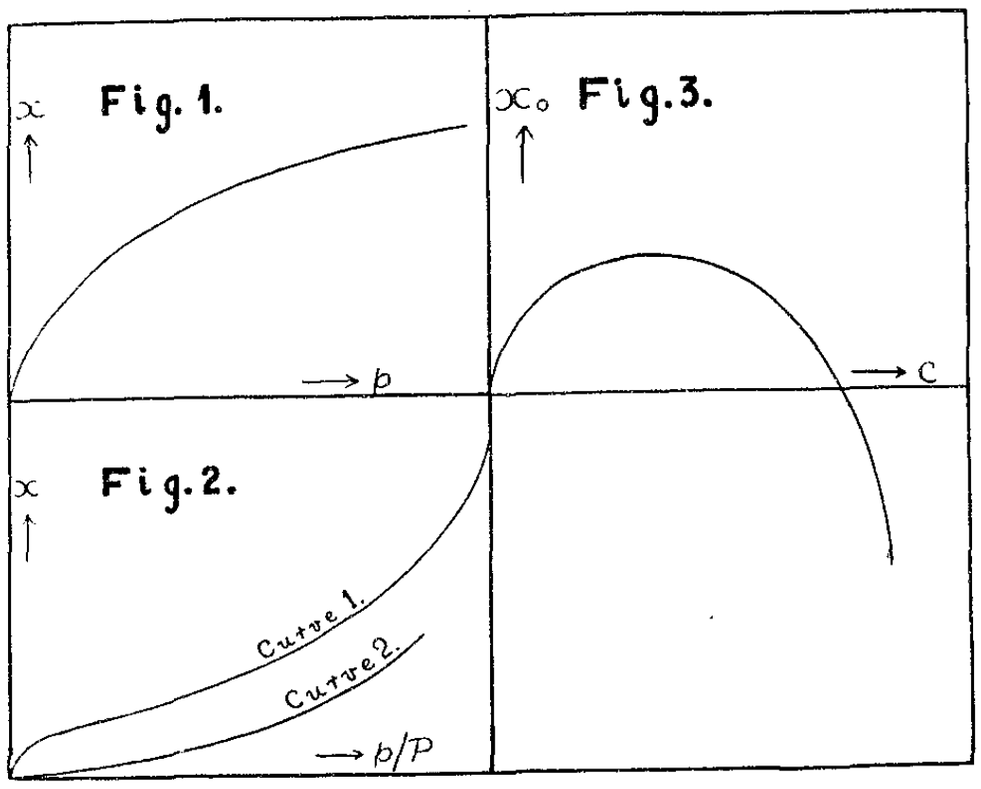
Berl and Schwebel[9] have combined Polanyi's equations with the "exponential" equation to find the quantity of steam required to expel a gas from an adsorbent. The agreement with experiment is excellent.

Considering the forces of adsorption to be of electrical origin Iliin[48] has obtained, by a method similar to that used by Eucken, a complicated expression for the amount adsorbed x in terms of the surface, temperature, etc., and a number of electrical quantities. This equation requires that the graph of $\log\left(x \cdot \frac{\epsilon - 1}{\epsilon}\right)$ where ϵ is the dielectric constant of the adsorbed gas, plotted against $\frac{\epsilon - 1}{\epsilon}$, should be a straight line. In this manner the equation is confirmed by the experimental results of Homfray and Titoff.

II. The Isotherm

A typical isotherm for adsorption from the gaseous phase is shown in Fig. 1. From this curve it is obvious that dx/dp approaches zero as p increases, d^2x/dp^2 being negative. The adsorption of vapours may be repre-

sented by one or other of the two curves of Fig. 2. For both these curves dx/dp increases as the partial pressure approaches its saturation value, but for curve 2 d^2x/dp^2 is positive, whilst for curve 1 d^2x/dp^2 passes from negative to positive values. Little information is available for the construction of isotherms illustrating adsorption from the liquid phase over any extended range of concentration, but what there is indicates that the curve is of the form shown in Fig. 3. It should be noted, however, that this curve shows the variation of x_o not x, with the concentration.



From a consideration of the curves shown above it seems clear that one equation cannot be expected to represent these various types of isotherms.

Empirical.

The equation $x = kc^{1/n}$, which is usually but erroneously called the "exponential," is perhaps the best known of all the equations which have been proposed to represent an adsorption isotherm. According to Firth,[19] De Saussure[94] in 1814 was the first to apply this equation to the adsorption of gases; its application was extended to solutions by Boedecker[10] in 1859, and in more recent years it has been used by hundreds of workers.

Experiment has shown that the exponent $1/n$ is always less than 1: hence dx/dc decreases as c increases, and d^2x/dc^2 is negative. Thus the equation may represent the isotherm for a gas shown in Fig. 1, but cannot represent any part of curve 1 of Fig. 2, while it is applicable only to the first portions of the other two isotherms. It would seem at first glance, therefore, that this equation does not agree very well with experimental data, but it should be noted that it can be applied to most adsorption phenomena in the low pressure or low concentration region, and as much of the experimental work which has

been carried out did not extend beyond this region, the equation was found to be of very general applicability. Above the region in which the equation may safely be used $1/n$ decreases with increasing pressure or concentration.

Consideration of a large amount of data has shown that the smaller the adsorbability of the gas the greater is $1/n$, a conclusion which agrees with Seeliger's[100] observation that $1/n \propto 1/T_c$ where T_c is the critical temperature of the adsorbate. It is also generally found that $1/n$ increases with increasing temperature; in fact, Berl and Schwebel[9] have shown from Polanyi's theory that $1/n \propto T$. Williams,[112] in a critical discussion of much data, has shown that at low concentrations $1/n$ approaches 1, i. e. the system obeys Henry's Law. All of these observations may be coordinated in the statement that the smaller the amount adsorbed the more nearly does $1/n$ approach 1. It is also found that $1/n$ increases with molecular complexity, runs parallel to the strength of solute acids, and is independent of the degree of dispersion of the adsorbent. k, on the other hand, increases with the degree of dispersion of the adsorbent and varies inversely as $l^{1/n}$, where l is the solubility of the solute.

Schmidt and Hinteler,[99] in applying the equation to organic vapours used it in the form $x = s(p/P)^{1/n}$, while a similar modification has been used by McGavack and Patrick,[67] viz $\frac{v}{\sigma^{1/n}} = k(p/P)^{1/n}$, where v is the volume of condensed vapour and σ is the surface tension.

According to Gurwitsch[31] the equation $x = k_0 + k_1 c^{1/n}$ agrees better with the results of experiment than the usual form, but the superiority of this equation has been disputed by Kolosovski.[49]. Ostwald and Izaguirre[75] have pointed out that the curves are identical, the only difference being in the disposition of the axes of reference.

It was found by Kroecker[51] that $dx/dm = \frac{\lambda(a - x)}{v}$ where a is the original amount of solute and λ is a constant. From this result Freundlich[22,23] deduced his "λ equation"

$$\lambda = \frac{v}{m} \log \frac{a}{a - x}$$

in which λ is independent of m, but is a function of a/v or C_0. He also found that

$$\lambda = \frac{v}{m} \log \frac{a}{a - x} = k_1 \left(\frac{a}{v}\right)^{k_2}$$

from which by expanding in series the "exponential" equation can be derived. In conjunction with Gibbs' equation (q.v.) it yields an expression for the variation of surface tension with concentration which agrees well with experiment. The λ equations have been criticised by McBain,[64] who concludes the system of λ formulae introduced recently by Freundlich to represent the amount of adsorption does not lead to any definite number characteristic of each set of substances, and further, its results are irreconcilable with each

other and with experiment. It should be noted, however, that in his argument McBain erroneously used zero instead of 2 as the limit when $a/c \rightarrow 1$ of the expression

$$\frac{d \log c}{d \log X/m} = \frac{(a - c) \log a/c}{(a - c) - c \log a/c}$$

Nevertheless, the λ equation is not unexceptionable, as is shown below. We have

$$\lambda = \frac{v}{m} \log \frac{a}{a-X}, \; c_o = \frac{a}{v}, \; c = \frac{a - X}{v}$$

$$X = mx = v(c_o - c)$$

Hence $$\lambda = \frac{x}{c_o - c} \log \frac{c_o}{c} = \frac{x}{c_o} \frac{\log c_o/c}{1 - c/c_o}$$

and $$\frac{d \log \lambda}{d \log c} = \frac{d \log x}{og c} - \frac{1}{\log c_o/c} + \frac{c/c_o}{1 - c/c_o}$$

Now if λ is independent of c when c_o is constant, as is claimed, then

$$\frac{d \log \lambda}{d \log c} = 0$$

and therefore

$$\frac{d \log x}{d \log c} = \frac{1}{\log c_o/c} - \frac{c/c_o}{1 - c/c_o}$$

$$= \frac{1}{-\log c/c_o} - \frac{c/c_o}{1 - c/c_o}$$

$$= \frac{1}{(1 - c/c_o) + \frac{1}{2}(1 - c/c_o)^2 + \frac{1}{3}(1 - c/c_o)^3 + \ldots} + 1 - \frac{1}{1 - c/c_o}$$

$$= \frac{1}{1 - c/c_o} - \frac{1}{2} - {}^{1}/_{12}(1 - c/c_o) - \ldots + 1 - \frac{1}{1 - c/c_o}$$

$$= \frac{1}{2} - {}^{1}/_{12}(1 - c/c_o) - \ldots\ldots$$

where all succeeding terms are negative. Now if adsorption is positive $c < c_o$ and therefore $0 < (1 - c/c_o) < 1$. Hence $\frac{d \log x}{d \log c}$, which is the 1/n of the exponential equation, has, for positive adsorption, a maximum value of $\frac{1}{2}$. This is quite contrary to experience. Moreover this value is obtained when $1 - c/c_o$ approaches zero, that is, when the adsorption is small, whereas it has already been mentioned that for small adsorption $1/n \rightarrow 1$.

Rakovski[88, 89] found that his isotherms for the absorption and desorption of water by starch could be adequately represented by the equation

$$p - k_1 = k_2 \sin(\sigma - k_3) + k_4 \sin(\sigma - k_5)$$

where $$\sigma = \frac{x}{s} \cdot \pi$$

This equation is discussed with relation to the two solution theory of gel structure. The same author[91] found that the adsorption of metallic hydroxides from solution by starch could be represented by the mass-action equation

$$\frac{x}{(M - x)(a - x)} = k$$

where M and a were the original amounts of starch and metallic hydroxide.

For the adsorption of gases the equation

$$x = k_1 p + k_2 p \log p$$

has been used by Kayser.[48] The curve of this equation is of the form of curve 1, Fig. 2.

Schmidt[95] used the equation $\log \frac{s}{s - x} = kc^{1/2}$, which agreed well with his experimental data.

Homfray[40] found that the equation $x = k_1 \log p + k_2$ which had previously been used to represent the adsorption of iodine and dyestuffs from solution, was quite inadequate as a representation of her data for gases.

Trouton[104] used the equation $(s - x)^2 = k(P - p)$ to express his results for the adsorption of water by cotton. From an examination of this equation it is obvious that it is applicable only to the upper portion (convex to the pressure axis) of the typical curve for a vapour.

Theoretical.

There have been a number of attempts to place the "exponential" equation on a sounder basis than that of mere empiricism, and some of these have met with a fair amount of success. Robertson[93] deduced the equation by considering adsorption to be a chemical reaction of the type $n_1 A + n_2 B \rightleftarrows n_3 AB$ and applying the Law of Mass Action, making certain assumptions as to the concentration of the adsorbent. This deduction has been criticised by Freundlich.[24] Kolthoff,[50] regarding the adsorption of ions by solids as analogous to the exchange of bases in permutite, has obtained the equation in which k depends on the solubility product of the two difficultly soluble salts and $1/n$ is inversely proportional to the valency of the adsorbed ion. What is perhaps the soundest deduction is due to Henry,[39] who has derived the equation by a consideration of the free surface energy changes of the bare and covered surfaces and by applying the Gibbs equation (q. v.). In his derivation $1/n$ has the theoretical significance of the ratio osmotic work done in the adsorption of x moles to total work in the adsorption of x moles, from which it follows that $1/n$ is always less than 1, and increases with increasing temperature.

Ostwald and Izaguirre[75] consider adsorption from solution to be essentially the adsorption of a layer of solution, so that two solvent layers are obtained between which the solute is distributed. By assuming that the amounts of solute and solvent adsorbed are given by the "exponential" equation, these authors deduce equations for the conditions:

(1) When the adsorption of solvent is neglected.

(2) When solvent is directly adsorbed.

(3) When solvent is found in the adsorbed phase as a result of the solvation of the solute.

(4) When solvent is found in the adsorbed phase according to (2) and (3).

On the assumption that adsorption may be attributed to the forces of physical attraction, chemical attraction, and physico-chemical attraction Gurwitsch[31] has shown that for solutions the equation to the isotherm must be $\varphi(x) = k + \psi(c)$. It is of interest to note that Gurwitsch's empirical equation (q. v.) has been derived by Zacharias[116] from the Nernst-Fick diffusion law, on the assumption that the resistance to diffusion varies as a power of the concentration.

Stadnikoff[101] distinguishes between four different types of adsorption, viz:

(1) Solution adsorption, which obeys Henry's Law. For example the distribution of potassium chromate between water and gelatin.

(2) Chemical adsorption, quantitatively expressed by the Law of Mass Action, for example the adsorption of acid by aniline black.

(3) (1) and (2) acting together.

(4) Exchange adsorption, as when an aniline salt adsorbs an acid other than that already combined in it. For such phenomena the ratio of the amount of the one adsorbed acid to its final concentration is directly proportional to the corresponding ratio for the other acid.

These considerations put forward by Stadnikoff are applicable only to solutions, and it is doubtful if all the phenomena considered can properly be included as adsorption.

Pavlov[77] has developed equations for chemical adsorption, distribution adsorption, and capillary adsorption, and has indicated how the three types may be distinguished. The use of the method is exemplified by its application to a study of the adsorption of acetic acid by charcoal.

Reichinstein[92] from his displacement principle has obtained an equation of similar form to those of Langmuir. Reichinstein's equation is, however, definitely limited to the isotherm.

The only theoretical treatment of the phenomena of hysteresis is that of Duhem,[15] whose mathematical analysis however, is too general to allow of quantitative comparison with existing data. Qualitatively his conclusions are in good agreement with the results of van Bemmelen.

Schmidt's[95] first equation for adsorption from solution

$$\log \frac{s}{s - x} - k_1 x = k_2 c,$$

was derived by an application of the mass action law, together with a number of assumptions of doubtful validity with regard to the physical conditions at the interface. The equation neglects the adsorption of solvent, and Arrhenius[2] has shown that the derivation is unsound for values of x approaching s. It has also been criticised by Marc.[61] The agreement with Schmidt's experimental data is fair, but probably no better than that of his empirical equation.

Arrhenius'[2] equation $\log_{10} \frac{s}{s - x} - .4343 \frac{x}{s} = kc$, is very similar to that

of Schmidt. According to this equation, however, $\frac{d \log x}{d \log c}$, i.e. 1/n of the exponential equation, approaches the value ½ as x decreases, which is contrary to the experimental evidence. It has been criticised by Schmidt[97] and Marc.[62]

By considering adsorption as a dynamic equilibrium between solute precipitated and solute dissolved, and assuming as before that the reaction coefficient varies with the amount adsorbed, Schmidt[96, 97] derived a second equation

$$\left(\frac{a - x}{v}\right)s = Cs = ke^{\frac{A(s-x)}{s}} \cdot x.$$

This equation yields a curve of the form shown in Fig. 1, and reduces to Williams' equation if s is replaced by an arbitrary constant. It also was adversely criticised by Marc,[62] following which Schmidt[98] gave two new derivations similar to the first but depending on the known laws of diffusion in solution. Realising, however, the error involved by neglecting the adsorption of solvent, Schmidt[99] has stated that the equation should not be used as a representation of an adsorption isotherm.

From a few simple assumptions Iliin[42] has obtained the equation $x = s(1 - e^{-kp})$, which is related to the equations of Schmidt, Arrhenius, and Langmuir.

Williams[113, 114] obtained thermodynamically the equation to the isotherm $\log x/c = k_1 + k_2x$. In the derivation of this equation higher terms of a series are neglected, so that it must be regarded as a first approximation only. Williams has shown that it agrees well with experimental data at low pressures, while Briggs[11] has shown that it may be successfully applied to gases above their critical temperatures at pressures up to 100 atmospheres, if a correction is made for the gas (obeying Boyle's Law) compressed in the pores of the adsorbent. Provided $1/x > k_2$, Williams' equation gives a curve of the type shown in Fig. 1.

The general equation to the isotherm obtained from Henry's[39] theory (q. v.) is not soluble, but for the adsorption of a single gas the equation becomes $x = k_1p\left(1 - \frac{x}{k_2}\right)^{k_3}$, which for small pressures is identical with Williams' equation.

The relationship between a number of the isothermal equations has recently been demonstrated by Gorbatschew,[30] who, by superimposing various simplifying assumptions on a few general relationships, has derived the equations of Langmuir, Reichinstein, Schmidt, Williams, and Henry, together with Freundlich's λ equations, and the "exponential" equation.

The lack of a complete mathematical interpretation of the isotherm has recently been expressed by McBain,[66] who believes that the "exponential" equation is still the best representation of the existing data.

III. The Isobar

Empirical.

Kayser[48] found that if v is the volume of adsorbed gas at temperature θ, then approximately, $v = k_1 + k_2\,\theta$

Ostwald[73] has used two equations, viz.

$$x = x_o + \frac{k}{T} \qquad \text{and } x = x_o + \frac{k}{T^3}.$$

Freundlich[25, 28] found that for not too high temperatures and pressures the log x, log p, curves at different temperatures spread out in a fan shaped diagram. In these circumstances

$$\log x_\theta = \log x_o - (\zeta - \xi \log p)\theta$$

where ζ and ξ are constants. By comparing this equation with the isobar obtained from the exponential equation by differentiating with respect to θ and putting $dx/dp = o$, it is found that

$$\xi = \frac{d\,1/n}{d\theta} \qquad \text{and } \zeta = -\frac{dk_\theta}{k\theta d\theta}$$

At higher temperatures $1/n$ approaches 1, and hence $\xi = o$, the equation to the isobar becoming $\log x_\theta = \log x_o - \zeta\theta$. This equation has also been used for adsorption from solution.

Theoretical.

Williams[113, 114] equation to the isostere (q. v.) is

$$\log \frac{RTx}{p} = \frac{k_1}{T} + k_2$$

If p is constant we obtain for the equation to the isobar

$$\log x = \frac{k_3}{T} + k_4 - \log T$$

Iliin[42] has recently obtained a relation between x and T of the form

$$x = k_1 e^{-k_2\sqrt{T}}$$

which gives fair agreement with the experimental data of Homfray and Titoff.

IV. The Isostere

Empirical.

By differentiating $x = kp^{1/n}$ with respect to θ and putting $dx/d\theta = o$, Freundlich[28] obtained for the equation of the isostere

$$\frac{d \log p}{d\theta} = n\,(\zeta - \xi \log p)$$

where ζ and ξ are the same constants that appear in Freundlich's equation for the isobar. As before at higher temperatures $\xi = o$ and thus the equation becomes

$$\log p\theta = \log p_o - \xi\theta$$

As a representation of her experimental data Homfray[40, 41] successfully used the Ramsay-Young vapour pressure law

$$\frac{T_o}{T_1} - \frac{T_o'}{T_1'} = R(T_o - T_o')$$

where T_1 and T_1' are the absolute temperatures corresponding to two selected pressures on any one isostere, and T_o and T_o' are the temperatures at which any saturated vapour exerts the same pressures. It is shown that this relationship may be derived from Bertrand's empirical vapour pressure formula $p = k_1\left(\frac{(T - x)}{T}\right)^{k_2}$, which itself expresses the isostere results. It is of interest to note that the Ramsay-Young equation may be derived from the Clapeyron equation by assuming that the molecular latent heat is independent of temperature. It may also be derived from van der Waals' equation.

Theoretical.

By equating two expressions for the change of energy consequent to the adsorption of 1 mole of gas obtained from the kinetic theory and the ordinary theory of attraction, Williams[113, 114] deduced the equation of the isostere to be

$$\log\frac{x}{c} = B + A/T$$

where B and A are independent of temperature. Although this equation is an approximation it is in good agreement with experimental data. In the deduction it is assumed, first, that the kinetic energy of a molecule is unchanged by adsorption, second, that $a(\delta - \sigma)$ is independent of temperature, where a is the area of the adsorbent, δ is the thickness of the adsorption layer, and σ is the diameter of an adsorbed molecule. From a long theoretical discussion a method is derived of placing the internal cohesion of gases, and of evaluating the range of molecular action and the thickness of the adsorbed layer. The values thus obtained are in good agreement with those obtained by other methods.

The isostere equation obtained from Henry's[39] theory (q. v.) is identical with that of Williams. Henry has also indicated a method of deriving this equation from Perrin's radiation hypothesis.

V. Rate of Adsorption

Whilst values from a few seconds to as many years have been recorded as representing the time required for the attainment of equilibrium in an adsorption system, there is a large amount of evidence to show that equilibrium is reached in a finite time. The curve showing the relation between x and t should therefore be of the form shown in Fig. 1, dx/dt decreasing with increasing t, and becoming zero at a finite value of t.

Empirical.

The equations of Mills and Thomson[70] and Mills and Takamine[69] are probably the first to be proposed for the representation of the rate of adsorp-

tion. These investigators found that the rate of adsorption of dyes from solution by textile fibres could be expressed in one of the forms:

$$y = A\alpha^t \pm B,\ y = A\alpha^t, \text{ or } y = A\ \alpha^t \pm B\ B^t$$

where y is the per cent dye remaining in the bath after time t, $A \pm B$ is the initial amount of dye (taken as 100), and α and B are constants.

For the adsorption of gases Bergter[8] has used the equation

$$x = \frac{k_1 t}{a + t} + \frac{k_2\ t,}{b + t}$$

as well as exponential equations of the type $x = k_1 + k_2 e^{k_3 t} + k_4 e^{k_5 t}$. Similar equations have also been used by other authors, including Rakovski,[90] and Bateman and Town.[5]

The best-known rate equation is probably that first used by Lagergren[52] $\frac{dx}{dt} = k(x_\infty - x)$, where x_∞ is the final value of x. This equation does not conform with the general requirements of the rate equation, and Gustaver[33] has pointed out that it is inapplicable to high concentrations, since it assumes the constancy during adsorption of the concentration.

Pickles[78] has used both for adsorption from a gas and from a liquid the equation

$$k = \frac{1}{t_2 - t_1} - \log\frac{a - x_1}{a - x_2} - .4343\ \frac{x_2 - x_1}{a}$$

where a is the original amount of adsorbate.

From their data, which are probably the most accurate figures known for the rate of adsorption of a gas, Burt and Bangham[12] have successfully used the equation $\log x = k_1 \log t + k_2$. Beyond the range in which this equation is applicable Bangham and Sever[4] have shown that the equation

$$\log\frac{x_\infty}{x_\infty - x} = k_1 t^{k_2}$$

may be used.

Zacharias,[117] using an equation due to Korner found that the rate of adsorption from solution was given by

$$\frac{dx}{dt} = k(c_o - x)\ (c - x)$$

Freundlich[26], [27] and his co-workers have represented the rate function by the "equations of negative auto-catalysis," either

$$\frac{dx}{dt} = 2kt(1 + bx)\ (1 - x)^2 \qquad \text{or} \qquad \frac{dx}{dt} = 2kt(1 + bx)\ (1 - x)$$

They have further found that the variation of k with temperature is given by Arrhenius' equation

$$\log k = -\frac{k_1}{T} + k_2,$$

and its variation with concentration by the equation $k = k_1x^{k_2}$

Dietl[14] has used these equations in preference to those of Zacharias and Lagergren and in preference to the equation

$$\frac{dx}{dt} = \frac{k(a - x)}{x},$$

and he has shown that one of them can be derived from the Nernst-Brunner diffusion equation

$$\frac{dx}{dt} = \frac{O\,D(a - x)}{\delta},$$

if δ, the diffusion layer, changes with time in the sense found by Moderstein and Fink for the kinetics of the contact process for the manufacture of sulphuric acid.

Recently Davis and Eyre[13] have claimed that for colloids the rate curve is discontinuous, each portion being represented by an equation of the type

$$x = k_1t + k_2t^2 + k_3t^3$$

The rate of evaporation from the very ill-defined system soil-water has been investigated by several workers, and various empirical formulæ have been proposed. A thorough analysis of this work has been made by Fisher,[20] who finds that the rate curve is discontinuous.

It will be noted that a number of these equations do not conform with the general requirements of the rate equation, and that for some of them $x \dashrightarrow \infty$ as $t \longrightarrow \infty$, which renders them applicable to a limited region only.

Theoretical.

By considering an adsorption system as a solid solution, and assuming the applicability of Fick's Law, McBain[65] derived an equation to represent the rate of adsorption. From a consideration of the properties of this equation, however, McBain concluded that any theory of arrested diffusion was untenable.

Marc,[63] assuming that the rate of adsorption in solution depends on the attractive force, the osmotic pressure of the solute, and the kinetic energy of the adsorbed molecules, writes

$$dx/dt = k_3x^{-k_1} - k_3 + k_2\,(a - x)$$

where the first term represents the effect due to the attractive force, the second term the kinetic energy of the adsorbed molecules and the third term the osmotic pressure of the solute. For values of x not too near $x\infty$, an approximate solution is given by

$$\frac{x^{k_1+1}}{t}\,(2x_\infty^{k_1} + k_2x^{k_1}) = k_3$$

This equation has also been used by Arendt.[1]

By assuming that the amount of adsorption is proportional to (1) the free surface, and (2) the total amount of adsorbate in the gaseous or liquid phase, Gustaver[33] obtained the equation

$$k = \frac{1}{t(a - x)\infty}\left(\log\frac{a - x}{x_\infty - x}\cdot\frac{x_\infty}{a}\right)$$

for adsorption from a liquid, a similar equation obtaining for the adsorption of a gas. These equations can also be deduced from Langmuir's theory.

Henry,[39] from the theory already discussed, has deduced the general equation for the rate of adsorption of one component (r) from a mixture of n gaseous components to be

$$\frac{dx_x}{dt} = k_1 p_r \left[1 - \frac{x_1}{s_1} - \frac{x_2}{s_2} \cdots\cdots - \frac{x_n}{s_n} \right]^{k_r} - k_2 x_r$$

Iliin[42] has obtained an equation $\frac{dc}{dt} = k_1 e^{-k_2 t}$ which agrees well with experimental results. This equation is of the same form as the empirical equations of Rakovski and Bergter.

VI. Heat of Adsorption

In this section, following Williams,[110] h is used to denote the heat of adsorption, defined as the ratio of the heat evolved to the gas adsorbed when only a very small quantity of gas is adsorbed; the total heat of adsorption will be, in general, $H = \int_{x_1}^{x_2} h_x \, . \, dx$. This integral can usually be obtained only by graphical or mechanical integration.

Empirical.

Whilst there are many early observations of heat effects accompanying adsorption, Freundlich[25] was the first to formulate equations for the heat of adsorption, distinguishing two kinds:

(1) Integral heat of adsorption, corresponding to heat of solution, evolved when a gas is brought into contact with just sufficient adsorbent to take it up.

(2) Differential heat of adsorption, evolved when one equilibrium condition is transferred to another. According to Freundlich this transformation can take place either isosterically (x constant) or isopneumatically (p constant). Combining the Clapeyron equation with his empirical equation to the isostere (q. v.) he obtained the equation

$$-h_x = \frac{nRT^2}{22410 \log_{10} e} (\zeta - \xi \log p)$$

for the differential heat of adsorption under isosteric conditions. Williams[110] has criticised the above classification as being confusing and erroneous, and has pointed out that the Clapeyron equation really refers to $(h)_{p,T}$. Arrhenius,[2] on the other hand, believes that the Clapeyron equation can be applied in the region where h does not vary greatly with p, since he supposes the adsorbate to behave as a liquid under its own saturated vapour.

Combining the Clapeyron equation with Bertrand's vapour pressure equation, Homfray[40, 41] obtained the equation $(h)_{p,T} = \frac{100xT}{T - x}$ where x is the amount of adsorbate expressed in per cent of adsorbent.

Lamb and Coolidge[53] from a study of the heat of adsorption of eleven organic vapours find that the heat of adsorption is given by $h = k_1 x^{k_2}$ where h

is the heat of adsorption per normal cubic centimetre of vapour and x is the number of cubic centimetres adsorbed. Since k_2 is approximately 1, the heat of adsorption decreases but slightly with increase in x. It is also found that the difference between total heat of adsorption and heat of evaporation is nearly constant for all liquids, and that these differences are closely proportional to the heats of compression under high pressures.

Katz and Holleman[47] have recently shown that for water and carbon from x = 5 to 81% (saturation = 93%) the variation in h is of the same order as the variation in free energy obtained from the equation

$$A = \frac{1252}{18} \log_{10} p/P.$$

Theoretical.

To Williams[108, 110, 111] is due the exact definition of h under different conditions, as follows:

(1) At equilibrium $(h)_T$; where adsorption proceeds with the vapour phase constantly in equilibrium with the adsorbed phase.

(2) At constant pressure, $(h)_{p,T}$; where the gas is adsorbed at constant but not necessarily equilibrium pressure.

(3) At constant volume $(h)_{v,T}$; where the total volume of the system is constant and the gas is adsorbed with a fall in pressure.

In a later paper[111] expressions are developed thermodynamically for $(h)_T$, $(h)_{p,T}$, and $(h)_{v,T}$. From these equations it follows as a first approximation that $(h)_{p,T} = (h)_{v,T} + RT$. The application of the equation for $(h)_{p,T}$ to Titoff's measurements leads to the conclusion that the surface area alters during adsorption.

Where a vapour is adsorbed as a liquid it is shown that $(h)_{p,T}$ is given approximately by the relation

$$(h)_{p,T} = RT^2 \left(\frac{\delta \log p/P}{\delta \log T} \right)_x$$

Expressions are also developed for the heat of immersion of a powder in a liquid when

(1) The powder is free from the adsorbate before immersion

(2) The powder is partially saturated before immersion

Corresponding to these two expressions two others are developed for similar conditions, but allowing for a change in the surface area of the adsorbent.

By finding the amount of work entailed in the formation of a single layer of gas on an adsorbent and integrating by reduction Eucken[17, 18] has obtained a simple equation which when coupled with the Second Law yields the simple result that the heat of adsorption per mole of gas is equal to the adsorption potential ϵ, defined as the amount of work involved in bringing a mole of gas from an infinite distance to the surface. Thus $H = \epsilon = Rk_2$, where k_2 is obtained from Eucken's adsorption equation (q. v.) for the total amount adsorbed. In a further discussion in which it is assumed that the adsorbing force is molecular attraction it is deduced that k_2 should vary as the square root of

(1) The boiling point of the gas
(2) van der Waals' a.
(3) The heat of evaporation of the adsorbed gas.

These expectations were realised.

By considering the orientation of the molecules resultant on dipolarity Lorentz and Lande[159] have also found the adsorption potential to be equal to the heat of adsorption. They have also shown from the theorem of corresponding states that the heat of adsorption per mole $H = R\Theta T_c$, where Θ is a universal constant $= \frac{k}{T_c}$, k being the constant of their adsorption equation (q. v.). k may also be obtained from a knowledge of the dipolar moment of the molecule. This application of the theorem of corresponding states only applies in the p, θ region where Henry's Law holds, and where $p \gg p_c$, and $\theta < \theta_c$.

Polanyi,[82] making the assumptions previously considered, found that $\epsilon_x = -RT \log p/P$, but differing from Eucken, set the heat of adsorption in a non condensible region $H = \epsilon_x + \sigma_x$, where σ_x is the molar heat of compression, equal to $a\delta$, where a is van der Waals' constant and δ is the density of the gas. For a gas in the condensible region the molar heat of evaporation (λ) must also be added, so that $H = \epsilon_x + \sigma_x + \lambda$.

On the assumption that the adsorbed vapour is compressed by the molecular forces Harkins[36] deduced th rmodynamically that for a saturated vapour $-H = E_s - E_i + \lambda_v$ where $-H$ is the heat of adsorption of sufficient vapour to form a liquid layer covering the solid surface,

λ is the heat of evaporation of unit volume,

E_s is the total surface energy of the solid,

and E_i is the total energy of the interface formed by the adsorption.

This equation, which really yields the heat of immersion, is deduced on the assumption that the surface area of the liquid is negligible in comparison with the area of the interface.

From the electrical theory of adsorption previously mentioned Iliin[43] has obtained for the heat of adsorption the equation

$$H = \frac{E_o^2}{8\pi}\left(\frac{\epsilon - 1}{\epsilon}\right)$$

where E_o is the tension of the electrical field in vacuo, and ϵ is the dielectric constant of the adsorbed gas. This equation is in good agreement with the experimental results of Homfray and Titoff. The same equation has been derived by Tarasoff,[102] who has also shown that $H\nu^2$ is a constant for a given adsorbent, where ν is the ionisation potential of the adsorbed gas.

Note on the Formulation of Adsorption Laws

For a theoretical investigation of the laws of adsorption two general methods are available; first, a development from the fundamental laws of thermodynamics, and second, a discussion of the kinetics of the adsorption process. Thermodynamic treatment has the great advantage that it does not

require a knowledge of the intimate mechanism of the process, and in particular it involves no assumptions with regard to molecular attraction. On the other hand no relation for the rate of adsorption can be obtained from thermodynamics alone. Kinetic treatment permits of the deduction of a rate of adsorption equation, but when an attempt is made to allow for the interaction of molecules the mathematics becomes so involved as to be impossible of solution.

The conditions obtaining in a solution are so complicated that it will probably be of little avail attempting to postulate any theory of adsorption from solution until our knowledge of the laws underlying adsorption from the gaseous phase is much more complete. It would seem that an adequate theory of gaseous adsorption should distinguish between a gas above and below its critical temperature. For the former there is no possibility of condensation to liquid, so that the adsorption layer would consist of gas, probably compressed, and would vary in thickness according to the pressure. For such conditions thermodynamic treatment has been successfully used, as witness the remarkable agreement between Briggs' experimental data and Williams' equation for the isotherm.

For a gas below the critical temperature a layer of gas would be expected at low pressures, but as the pressure is increased condensation might occur, with the formation of a liquid film. If the adsorbent were porous a simultaneous condensation would take place in the pores,[60] obeying, probably, quite other laws. Anderson, Zsigmondy, Fisher, Trouton, and Gustaver believe that this condensation takes place according to Kelvin's equation

$$r = \frac{2\sigma D_v}{D_L P \log P/p}$$

where r is the radius of the liquid meniscus,

D_v is the vapour density at pressure P,

and D_L is the liquid density.

Wilson[115] considers that this equation is only applicable to pores of radius greater than 5×10^{-8} centimetres. It may well be, however, that the breakdown for very small pores is due not so much to an imperfection in the equation as to the insertion of the wrong value of σ in it, since it is not permissible to assume that the surface tension of such very thin films is identical with that of the liquid in bulk.

Most of the evidence with regard to an *adsorbed* liquid film (as distinct from a column of liquid in a pore) tends to show that it is very thin. Thus Katz[45, 46] has shown from the equation $F = RT \log p/P$, where F is the molecular attraction, that the force of attraction diminishes rapidly with increase of thickness, whilst Hatschek[38] by means of the Einstein-Hatschek viscosity equation has shown that the thickness of the adsorbed film on the spheres of a suspension in sodium chloride solutions is of the order 8×10^{-8} centimetres, which is about twice the diameter of a water molecule. On the other hand, reference must be made to some recent work of Hardy,[34] which shows that a surface may exert a specific effect through a layer of liquid probably some hundreds of molecules thick. For a reconciliation of these divergent views we must look to the future.

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SOCIÉTÉ DE CHIMIE INDUSTRIELLE
28, Rue St-Dominique
ANNULÉ
PARIS (7e)

ADSORPTION AND HEAT OF ADSORPTION OF AMMONIA GAS ON METALLIC CATALYSTS*

BY WALTER A. DEW AND HUGH S. TAYLOR

In order that a more extensive knowledge might be acquired of the relationship existing between heat of activation, adsorption, heats of adsorption and catalytic activity, measurements of the specific adsorption and the heats of adsorption of ammonia gas on copper, nickel and iron catalysts have been made. These determinations combined in one operation three lines of investigation which had been previously carried out in this laboratory. Adsorption measurements have been made such as those of Taylor and Burns[1] while isotherms for ammonia and hydrogen corresponding to the investigations of Gauger and Taylor[2] and integral and differential heats of adsorption were measured in the same manner as did Beebe and Taylor.[3]

Although it is known that substances which possess a great adsorbing power are not necessarily the best catalysts,[4] yet much emphasis has been placed upon the determination of specific adsorption of catalytic agents as a criterion for their activity in certain reactions and there seems to exist an intimate relationship between the specific adsorption and catalytic activity.[5] Assuming some relationship to exist between the adsorbent and the adsorbed gas it was thought that adsorption measurements upon various catalysts which cause the decomposition of ammonia might reveal some data of fundamental nature concerning the reaction,

$$2NH_3 = N_2 + 3H_2$$

That iron at elevated temperatures causes this decomposition to take place was first investigated by Ramsay and Young[6] and, subsequently, more thoroughly by Beilby and Henderson[7] who, in addition, studied the action of ammonia on nickel, copper, silver, gold, and platinum, and various other metals and alloys at temperatures lower than their melting points. The latter authors concluded that the decomposition of ammonia is due to a nitride formation occurring when excess ammonia is present.

Although no measurements have been made of the specific adsorption of ammonia gas for any of the metals previously mentioned it has been found by Taylor and Burns[8] that iron adsorbs hydrogen gas to a certain extent and that nitrogen gas is not measurably adsorbed. Nickel and copper have been in-

* Contribution from the Laboratory of Physical Chemistry, Princeton University, N. J.

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vestigated more thoroughly and the heats of adsorption of hydrogen determined by Beebe and Taylor[1] under various conditions. These metals also show no measurable adsorptive capacity toward nitrogen. In addition, a few adsorption measurements were made on a supported sodium catalyst. Catalysts from several groups of metals were thus represented. Some work previously carried out in this laboratory by Dr. A. F. Benton on the adsorption of ammonia gas by a 50-50 mixture of iron-molybdenum has been incorporated also with these measurements.

Of the metals examined, sodium is known to react with ammonia at 300°-400°C. to produce sodamide[2] according to the equation

$$2Na + 2NH_3 = 2NaNH_2 + H_2.$$

Since it is a very reactive metal it might be expected that irreversible adsorption alone would be observed. At the temperature at which the determination was made, however, reversible adsorption occurred. The remaining metals would be expected to show reversible adsorptions and this was found to be the case.

The relationship existing between the heat of activation and heat of adsorption has been clearly stated by C. N. Hinshelwood[3] as follows:

$$E_o = E_t + \lambda' - \lambda$$

where E_o = the observed heat of activation
E_t = the true heat of activation
λ' = the heat of desorption
λ = the heat of adsorption

and the value for λ' for hydrogen on catalytic nickel has been measured by Beebe and Taylor[4] and also by Foresti[5] and more recently by Fryling[6] who extended the work to promoted nickel catalysts at low pressures. Beebe and Taylor also measured the heat of adsorption of hydrogen on copper.

Experimental

METHODS OF MEASUREMENT:—In carrying out the adsorption measurements the apparatus employed was entirely similar to that used and described by Pease and the temperatures employed were 0°, 110°, 218°, 305° and 444.6°C. which were attained by the use of ice and water, boiling toluene, naphthalene, acetanilide and sulphur respectively. The temperature regulation in the case of the determinations on iron-molybdenum was achieved by water at 25°C. and 100°C. and by an electrically heated air bath at the higher temperatures. Evacuation in this latter case was accomplished at 500°C.

Evacuation at room temperature was employed for sodium, and a temperature of 218° was commonly used for copper, nickel and iron except where determinations were carried out at higher temperatures in which case the tube was evacuated at the higher temperature.

[1] loc. cit.
[2] A. W. Titherley: J. Chem. Soc., **65**, 504 (1894).
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Nitrogen was used as the reference gas by which the free space of the bulb was obtained, since it was found by Taylor and Burns to be unadsorbed.

When heat of adsorption measurements were made a catalyst tube exactly similar to the one employed by Beebe and Taylor, with an estimated capacity of about 50 cc. when empty, was substituted for the catalyst tube previously used. Catalyst transfer from a separate reduction tube was accomplished in an atmosphere of inert gas. The heating coil used was made of platinum-palladium wire of 0.10 mm. diameter and 44.3 cm. in length and had a resistance of 10.005 ohms. The coil was insulated to prevent short circuiting as described by Beebe and Taylor. The leads, welded to the heating coil, were made of stout wire as short as possible and terminated in mercury cups by means of which connection was made to the calibration apparatus. Calibration was carried out exactly as described by Beebe and Taylor, the 10 ohms heating coil being employed. Care was exercised to keep the leads and mercury cups well below the surface of the ice bath to prevent any loss of heat by conduction.

For evacuation, the catalyst tube was heated by means of an air bath, the de Khotinsky joint being protected by a small lead tube wrapped about it several times, through which tube water circulated. In the case of copper, evacuation was carried out at 200°C., but 300°C. was employed for both nickel and iron. A Dewar flask filled with water and cracked ice was placed about the catalyst tube after evacuation was complete and all determinations of heats of adsorption were made at 0°C.

Nitrogen was employed as a reference gas, since it was found by Beebe and Taylor to be unadsorbed and consequently a suitable gas by which thermal effects, due to compression of the gas entering the calorimeter and to cooling from room temperature, could be observed. Calibration measurements were carried out, however, with the catalyst chamber filled with ammonia gas. It was found necessary also to introduce a correction factor for the effects noted above due to the fact that nitrogen is a diatomic gas and ammonia is a tetratomic gas. These corrections will be fully considered later.

CATALYST PREPARATION:—Sodium was prepared by distilling the metal in vacuo and condensing it upon glass beads in the reaction tube. This was accomplished by drawing the tube out into two bulbs quite similar to an old-fashioned hour glass. Into the lower one was introduced a weighed piece of sodium, and the upper was filled with glass beads. The upper bulb was sealed to a capillary tube which was attached to the apparatus. A Toepler pump was used to evacuate the system as it was heated. Distillation was carried out at 400-450°C. and a silvery mirror of sodium was deposited on the glass beads. The tube containing the catalyst was then sealed off and the weight of the sodium which had distilled was obtained.

Copper 2 was prepared from Kahlbaum's "brown label" copper oxide ground to granules of about 2 mm. in size. Reduction was carried out at 145-150°C. for a period of six days in a stream of pure dry hydrogen. The end point of the reduction was indicated when no increase was observed in the

weight of a calcium chloride tube through which the effluent hydrogen was allowed to pass for an hour.

Copper A was prepared in the same manner as Copper 2 except that the temperature of reduction was maintained at 140-145°C. for a period of twenty-two days. At the end of that time the reduction was still producing 0.6 mg. of water vapor per hour.

Nickel 8 was prepared by igniting the pure nitrate in a casserole over a small flame, transfering this material to the reduction tube, calcining at 300°C. and reducing in a stream of hydrogen as described by Gauger and Taylro for the unsupported catalyst which they used.

Nickel A was prepared in the same manner as Nickel 8 the reduction temperature being maintained at 285-300°C. Reduction was slow at that temperature, for at the end of fifty days 0.4 mgm. of water vapor was being formed per hour. Noticeable contraction of the mass was observed at the end of the reduction period.

Iron 1 was prepared by dissolving pure soft iron turnings in nitric acid. The resulting nitrate solution was filtered, evaporated to dryness and ignited slowly on a sand bath. Reduction was carried out in a stream of dry electrolytic hydrogen at a temperature of about 600°C. for a period of sixteen days.

Iron A was prepared exactly as Iron 1 except that the reduction temperature was maintained at 440 460°C. At the end of thirty days no formation of water was observed and reduction was considered complete.

Iron-molybdenum was prepared by dissolving 113 g. of soft iron in equal volumes of concentrated nitric acid and water, adding to this solution 227 g. of ammonium molybdate dissolved in water. The combined solution was evaporated to dryness, stirring constantly toward the end. It was then ignited on a sand bath to drive off excess nitric acid. Reduction was carried out in hydrogen at 445° for 20 hours, at 500° for 10 hours, and at 530° for 26 hours. At the end of this time reduction was not absolutely complete, water being formed at the rate of 18 mg. per hour.

PREPARATION OF GASES:—Nitrogen was obtained by passing tank nitrogen through a purifier, containing a solution of ammoniacal cuprous carbonate, to remove oxygen, washing with sulphuric acid, then passing over hot copper to remove traces of oxygen, and drying by passing through calcium chloride.

Hydrogen was prepared electrolytically as described by Pease.[1]

Ammonia was prepared by gently warming concentrated aqua ammonia in a large flask and passing the gas through drying towers filled with soda lime and potassium hydroxide. Before introducing the gas into the measuring burette it was tested for its solubility in water, portions of the gas being taken which were completely soluble in water.

Experimental Results

ADSORPTION DATA:—In Table I are the values obtained for the adsorption of hydrogen and ammonia on the various catalysts at the several temperatures mentioned. The specific adsorption or the cc. of gas adsorbed by one gram of

[1] Pease: J. Am. Chem. Soc., **45**, 1196 (1923).

metal is noted instead of the volume adsorbed by one volume of catalyst. In order to compare these values, therefore, with those given by other observers[1] it is only necessary to multiply the value of the specific adsorption by the density of the metal catalyst to obtain the volume adsorbed by one volume of the metal. These values were checked so that all results were reproducible with the sample examined.

TABLE I

c.c. Gas required to fill bulb
Reduced to N. T. P.

Metal	Weight	Gas	0°	110°	218°	305°	444.6°
Sodium	1.7153	N_2	7.89	—	—	—	—
		NH_3	8.16	—	—	—	—
Copper	35.8282	N_2	24.72	16.78	13.36	—	—
		H_2	30.28	21.58	16.71	—	—
		NH_3	41.12	23.48	17.38	—	—
Nickel	16.8430	N_2	27.69	19.92	15.75	14.41	—
		NH_3	42.13	27.62	17.43	15.51	7.83
Iron	10.7632	N_2	17.72	12.84	10.19	8.99	7.43
		H_2	17.80	12.87	10.40	9.19	7.61
		NH_3	19.60	13.56	10.58	9.08	7.28

Specific Adsorption
c.c. gas taken up by 1 gram of metal

Sodium	N_2	0.0	—	—	—	—
	NH_3	0.16	—	—	—	—
Copper	N_2	0.00	0.0	0.0	—	—
	H_2	0.155	0.134	0.093	—	—
	NH_3	0.458	0.187	0.112	—	—
Nickel	N_2	0.00	0.0	0.0	0.0	—
	NH_3	0.875	0.0457	0.100	0.065	—
Iron	N_2	0.0	0.0	0.0	0.0	0.0
	H_2	0.0074	0.0028	0.0195	0.0116	—
	NH_3	0.175	0.0669	0.036	0.0084	—

[1] Taylor and Burns: J. Am. Chem. Soc., **43**, 1277 (1921); Gauger and Taylor: **45**, 923 (1923); Hempel and Thiele: Z. anorg. Chem., **11**, 93 (1896); Mayer and Altmayer: Ber., **41**, 3062 (1908); Troost and Hautefeuille: Compt. rend., **80**, 788 (1875).

COPPER. Upon comparison of the values obtained for the adsorption of hydrogen by copper (namely 1.381 vols. per 1 vol. of copper) with the values obtained by Taylor and Burns (less than 0.05 vols. per vol. of copper) it is seen that the amount adsorbed is some 200 times as great at 110° and is more than 5 times as great as that observed by Pease who obtained 0.232 vol. per vol. of copper but is about one-third of that obtained by Beebe and Taylor, who found 3.8 vols. per vol. of copper.

The comparatively large adsorption of hydrogen observed by copper is probably due to the fact that the temperature of reduction was low.

The value obtained for the specific adsorption of ammonia on copper is large compared to the hydrogen value showing that the sample investigated possessed good adsorptive power for ammonia, the value being readily measurable at all temperatures employed. In no case was there any indication of decomposition of the ammonia by the copper at the three temperatures employed as shown by the observation that the ammonia gas when pumped off was completely soluble in water.

NICKEL. Nickel was observed to adsorb ammonia very strongly, giving a value which is nearly twice as large as that obtained for copper at 0°. At 213°, however, the initial volume adsorbed began to decrease slowly, indicating plainly that decomposition of the ammonia was taking place.* This decrease was not noticeable in the first five minutes, after which time it fell away until a constant value was reached. The gas which was pumped off the catalyst was tested qualitatively for hydrogen which was found to be present.

At 305° the amount of decomposition of ammonia was slight and took several minutes before it became measurable, which was probably due to the small adsorption of the ammonia by the nickel.

IRON. The values obtained for the adsorption of hydrogen were found to be small, checking closely with those obtained by Taylor and Burns.[1]

Adsorption of ammonia was much larger than that of hydrogen but not so large as might be expected were total adsorptive capacity the only criterion of activity. This may be attributed to the high temperature at which the iron was reduced and, as will be indicated later, this point of view is substantiated for Iron A on which heat of adsorption measurements were made. This sample showed adsorptions that were nearly as large as Nickel 8. These measurements indicate by contrast the importance of maintaining low temperatures in the preparation of unsupported catalytic materials if they are to have a high adsorptive capacity.

In making the measurements no decomposition of ammonia was observed at any temperature until 444.6°C. was reached. Considerable decomposition of the gas took place at this temperature as was indicated by collecting 9.8 c.c. of the desorbed gas of which only 4.1 cc. was soluble in water.

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* Note:—It should be noted here that the initial value was taken as that of true adsorption instead of a value taken when the reading of the burette became constant as was the case at lower temperatures. In taking the initial value no doubt some error is involved since it is not known how rapidly the ammonia is decomposed at those temperatures.

[1] Taylor and Burns: J. Am. Chem. Soc., **43**, 1280 (1921).

Adsorption Isotherm of NH_3 on Copper at 218°:—Since copper was found not to decompose ammonia at 218° it was decided to obtain an isotherm curve which would indicate the nature of the ammonia adsorption at 218°. The following diagram, Fig. 1, indicates very clearly the relationships which are found to exist between the pressure and the volume adsorbed. It will be observed that there is strong adsorption at low pressures. At 400 mm. the adsorption has reached 3.4 cc., whilst an additional 400 mm. pressure results only in the adsorption of a further 0.6cc. This indicates approaching saturation of the surface.

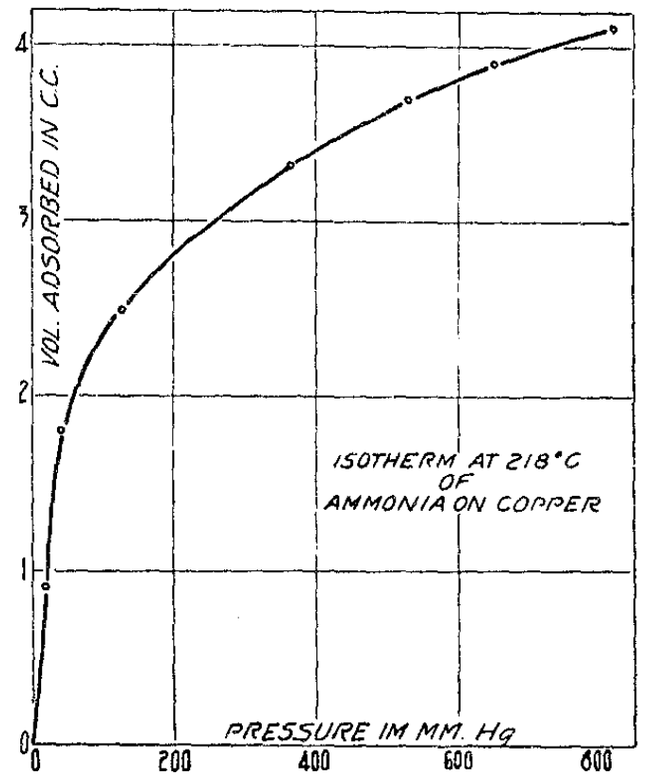


FIG. 1

Isotherms for NH_3 on Nickel at 110° and 0°C:—The accompanying curves, Figs. 2 and 3 indicate the variation of the adsorption of ammonia gas with pressure at the two temperatures. It may be observed that the NH_3 curve on nickel at 110°C. is very similar to that obtained on copper which has just been described. At 0°C., however, the adsorption of ammonia at the lower pressures is quite marked but there is little evidence of approaching saturation even at the highest pressures studied.

IRON-MOLYBDENUM. The results of the measurements of adsorption on this catalyst sample may be briefly summarized in a table.

TABLE II

Catalyst	wt. in grams	Gas	cc. Gas required to fill bulb at N. T. P.		Specific Adsorption	
			25°	100°	25°	100°
Iron Molybdenum	125	H_2	69.30	55.2	0.0032	0.0
		NH_3	357.4	—	2.30	—

Benton says: "No solution of hydrogen or chemical reaction occurred at 25° since equilibrium was always quickly reached and the curves coincide for introducing and withdrawing the gas, all the hydrogen being recovered. The same is true at 100° except that 0.37 cc. of hydrogen were not recovered and therefore presumably reacted with the unreduced oxide.

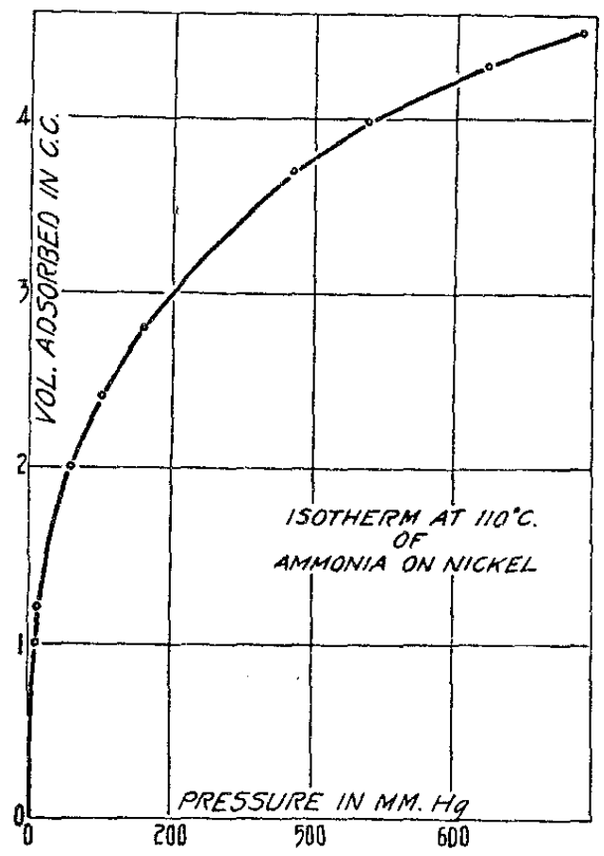


FIG. 2

"If any hydrogen is adsorbed at 25° or 100° it must be roughly proportional to the pressure. If it be assumed, however, that no hydrogen is adsorbed at 100° the free space in the bulb is $55.2 \times \frac{372.2}{273} = 75.2$ cc. and the volume of gas required to fill this space at 25° would be 68.9 cc. Actually, however, 69.3 cc. of hydrogen at 25° were needed. Hence the minimum adsorption of hydrogen at 25° was 0.40 cc. which is the order of magnitude obtained by Taylor and Burns for hydrogen on iron.

"In any case, since the volume adsorbed cannot possibly vary inversely as the absolute temperature, these calculations show that Fe-Mo adsorbs scarcely any hydrogen at 25° and 100° and, therefore, hydrogen determinations can be used to determine the free space in the bulb, especially as the ammonia adsorptions are large." The isotherm given, Fig. 4, indicates that the amount of ammonia adsorbed at low pressures is very large.

Heats of Adsorption.—A slight deviation from the method used by Beebe and Taylor was necessitated by the fact that nitrogen, a diatomic gas, was

employed to determine the heat effects previously mentioned, whereas ammonia is a tetratomic gas. This can probably be illustrated best by an example or typical calculation as in the case of

NICKEL A. Determinations of Free Space and Heat Effects employing the average of Runs 1 and 2.

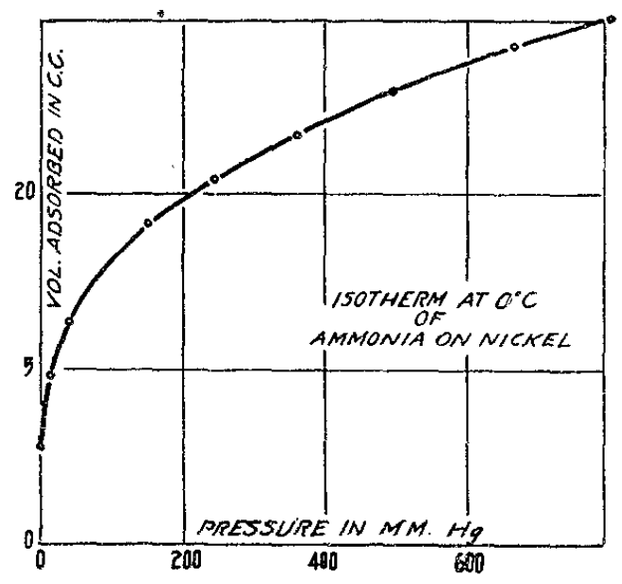


FIG. 3

1		2	
Maximum Temperature	0.210	Maximum Temperature	0.200
Initial "	0.160	Initial "	0.155
Observed " Rise	0.050	Observed " Rise	0.055

Average Observed Temperature Rise ..... 0.053° in 3 minutes

Observed Temperature Rise	0.053
1st minute correction	0.001
2nd " "	0.002
3rd " "	0.002
True Temperature Rise	0.058
Average Volume N_2 Introduced	39.93 cc. N. T. P.

Mol. Heat of $NH_3 = 0.5202 \times 17 = 8.84$
" " " $N_2 = 0.2438 \times 28 = 6.82$

Amount of heat N_2 would liberate in cooling from 21.1°C. to 0° is given thus:

$$N_2 \text{ heat capacity} = \frac{39.93}{22{,}400} \times \frac{6.82}{13.75} \times 21.10^\circ = 0.019^\circ.$$

where 13.75 calories = Heat capacity of Calorimeter.
Total Temperature Rise = 0.058°
N_2 heat capacity = 0.019.

Hence, by subtraction, the heat effect due to compression = 0.039°.

To find the NH_3 equivalent of the nitrogen value for heat capacity of the gas, we have, $0.019° \times \frac{8.84}{6.82} = NH_3$ equivalent, or $0.024°$, due to heat capacity of the ammonia. Hence the total effect due to introducing 39.93 ccs. NH_3 is $0.024 + 0.039 = 0.063°C$. The remaining calculations are similar to those of Beebe and Taylor.

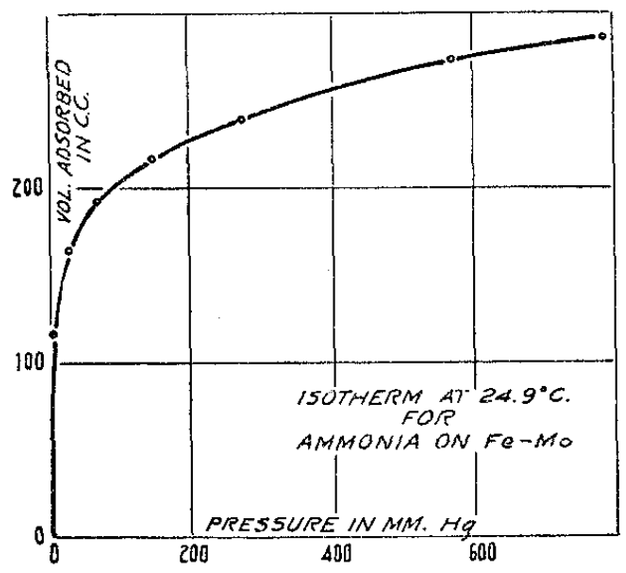


FIG. 4

Copper:—This catalyst was prepared as previously described in order to reproduce the sample upon which adsorption measurements alone were made. It is of interest to note the extent of this reproducibility. The following table reveals that the average volume of ammonia taken up by the sample was 17.37 cc. which gives a specific adsorption of 0.4958 cc. per gram for copper A as compared with 0.4577 cc. per gram for copper 2. This shows a reproducibility of about 6 per cent.

The results obtained for the heat of adsorption on copper may be summarized most conveniently in two tables, the first showing determinations of the integral heats of adsorption and the second showing heats of adsorption at various partial pressures.

TABLE III

Integral Heat of Adsorption

Copper A. Weight 35.03 grams

Determination	c.c. adsorbed (0, 760)	Temp. Rise	
1	17.50	0.455	7,711
2	17.25	0.449	7,720

The heat capacity of the calorimeter was found to be 13.24 calories.

TABLE IV

Differential Heat of Adsorption. (Q at Partial Pressure).

Determination	Pressure in m.m.	cc. adsorbed (0, 760)	Temp. Rise	λ
1	178.5	9.53	0.291	9,056
2	199	7.60	0.224	8,743
3	155	7.00	0.218	9,236
4	192	9.13	0.266	8,663

Nickel A:—The catalyst used here was prepared in order that it might be as nearly as possible of the same activity as the first sample on which adsorption measurements were made. Though greatest care was exercised the latter catalyst was about 14 per cent less active in ammonia adsorption than the first. One run was made to determine the integral heat of adsorption of hydrogen on this catalyst. A value of 14,960 calories was obtained which checks very well with those obtained by Beebe and Taylor.

The results of the integral heat of adsorption measurements of ammonia on nickel may be tabulated as follows:

TABLE V

Integral Heat of Adsorption of Ammonia on Nickel

Determination	c.c. adsorbed (0, 760)	Temperature Rise	λ
1	21.19	0.772	11,220
2	21.00	0.789	11,570

The heat capacity of the catalyst and calorimeter was 13.75 calories.

TABLE VI

Differential Heats of Adsorption on Nickel A

Determination	Initial Pressure	Final Pressure	c.c. Vol. gas Adsorbed (0, 760)	$T-T^\circ$	λ
1	0	183.5	11.90	0.445	11,520
2	0	198	13.94	0.446	9,854
3	0	210	11.79	0.412	10,760
3A	210	758	6.82	0.170	7,677
4	0	141	10.03	0.360	11,060
4A	141	759	5.06	0.186	11,320
5	0	62.5	6.50	0.240	11,370
5A	62.5	212	3.77	0.116	9,477
5B	212	465	3.40	0.087	7,881
5C	465	759	3.46	0.067	5,964
6	0	89	7.73	0.282	11,240
6A	89	224.5	5.03	0.085	8,640
6B	224.5	511.5	3.90	0.089	7,029
6C	511.5	756	2.54	0.058	7,033

T is the highest temperature observed plus corrections.
T_0 is the initial temperature.

It will be observed that the heat of adsorption of ammonia at low pressures is about 11,300 calories and gradually decreases to about 7,000 calories as the pressure increases.

Iron A. In order that a catalyst of greater adsorptive capacity might be obtained, the reduction temperature was maintained as low as possible. The sample examined weighed 49.35 grams and showed a specific adsorption of about 0.5 cc. per gram which is about three times as large as that of iron 1 at 0°C. It is approximately thirty per cent less, however, than the specific adsorption of Nickel A at 0°C. The heat capacity of the catalyst and calorimeter in these measurements was 17.98 calories. No determinations were made of the integral heat of adsorption. Table VII gives the differential heats of adsorption.

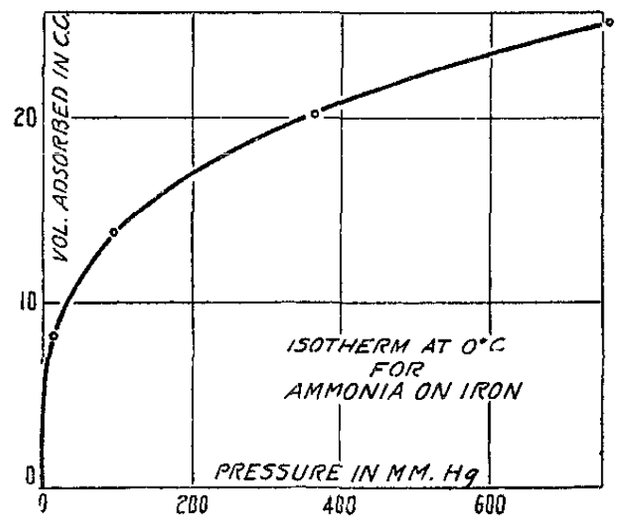


FIG. 5

TABLE VII

Differential Heats of Adsorption in Iron A

Determination	Initial Pressure	Final Pressure	cc. Vol. gas adsorbed (0, 760)	$T-T_0$	λ
1	0	16	8.05	0.320	16,010
1A	16	97.5	5.61	0.152	10,910
1B	97.5	368	6.84	0.155	9,127
1C	368	756	5.61	0.113	8,113
2	0	16	7.56	0.292	15,580
2A	16	102.5	5.99	0.142	9,548
2B	102.5	368	5.02	0.122	9,788
2C	368	756	4.43	0.088	8,008

At low pressures it will be seen that the heat of adsorption of ammonia on iron is about 16,000 calories, a value much larger than that obtained in the case of nickel.

Employing the value of 38.22 cc. for free space obtained by using nitrogen it is possible to obtain an isotherm curve (Fig. 5) for ammonia on iron at 0°C. It may be noticed that the curve obtained is quite similar to the isotherm of ammonia on nickel at the same temperature.

Discussion of Results

All the catalysts studied have been shown to possess adsorptive capacity for ammonia at the temperatures studied and the adsorption has been shown to be reversible in the lower range of temperatures employed. At the higher temperatures decomposition of ammonia occurs.

From the known reactivity of ammonia with sodium to yield sodamide[1] and from the presence of nitrogen in samples of nickel and iron which have been used to decompose ammonia, we may conclude that the ammonia is attached to the metal surface[2] by a metal-nitrogen linkage. At low temperatures the ammonia may be removed intact. As the temperature is raised, however, internal rearrangements in the adsorbed ammonia molecule may occur. In the case of sodium, this leads to a definite compound, $NaNH_2$, with elimination of one atom of hydrogen from each ammonia molecule. In the case of the other metals such compounds are not identifiable but it is found that the hydrogen comes off in such cases prior to the nitrogen, leaving the metal charged with this latter, not however in definite stoichiometric proportions.

Assuming that the whole surface is not uniformly active and that it is the fraction of the surface having the strongest adsorptive capacity which is the most active catalytically, it is of interest to note that the heats of adsorption at very low partial pressures stand in the order (1) iron, 16,000 calories; (2) nickel, 11,300 calories; (3) copper, 8,700 calories. It is these values which are to be inserted for λ in the expression

$$E_o = E_t + \lambda' - \lambda$$

previously given. This would indicate that the apparent heat of activation, E_o, would be most markedly affected by the heat of adsorption in the case of iron, least in the case of copper. There is, however, another point of view in this respect. The higher heat of adsorption of ammonia on iron means that it is possible to raise an adsorbed molecule to a much higher temperature on an active iron spot than on an active copper spot. There is thus offered a greater probability of interaction between the metal atom and the ammonia molecule in the case of iron than in the case of copper. It is possible that the higher activity of iron as a catalyst for ammonia decomposition is to be associated with this observation. Expressed otherwise, there is the possibility of inelastic collisions between impinging ammonia molecules and the metal surface at much higher temperatures in the case of iron than in the case of copper, which is equivalent to saying that the 'active mass' of ammonia is greatest in contact with iron at the temperature in question.

Summary

(1) Values for the specific adsorption of ammonia and hydrogen gases were determined for sodium, copper, nickel, iron, and a 50-50 mixture of iron molybdenum at various temperatures.

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[1] Titherley: J. Chem. Soc., **65**, 504 (1894).

[2] Beilby and Henderson: J. Chem. Soc., **79**, 1250 (1901); Fowler: **79**, 288 (1901); White and Kirschbaum: J. Am. Chem. Soc., **28**, 1347 (1906).

(2) Adsorption isotherm curves were determined for ammonia on copper at 218°, on nickel at 110° and 0°, on iron molybdenum at 25° and on iron at 0°.

(3) Integral heats of adsorption for ammonia gas at 0°C. on copper, and nickel have been determined.

(4) Differential heats of adsorption for ammonia gas at 0°C. on copper, nickel, and iron have been tabulated.

(5) The effect of temperature on the preparation of unsupported active catalyst samples has been emphasized.

(6) An apparent relationship between heat of adsorption and catalytic activity has been presented in the case of the reaction $2NH_3 = N_2 + 3H_2$.

THE NEUTRAL SALT EFFECT*

BY L. E. BOWE

Historical

In 1888 Spohr[1] and in 1889 Arrhenius[2], in experimenting on the catalysis of the hydrolysis of sugar and ethyl acetate, found that the addition of some neutral salts increased the rate of inversion of cane sugar and the hydrolysis of ethyl acetate in the presence of a constant amount of acid. They found that the more dilute the acid, the greater was the effect of the added salt. Arrhenius[3] offered several explanations for this effect, some of which still find favor today. He attributed the increase in velocity to one or more of three causes.

1. The increase in the ionization of the acid.
2. The increased ionization of the water.
3. The shift in the equilibrium "inactive $\leftrightharpoons$ active" molecules, to the right on the addition of neutral salts.

Euler[4], working on the same problem, attributes the "salt effect" to the fact that water reacts through its ions and that salts affect reactions by changing the dissociation constant of the water. This is still believed by some to be one of the factors in this complicated problem. Euler's theory is merely an enlargement of that of Arrhenius.

Since that time considerable work has been done on this question and several theories have been suggested, some of which will be enumerated here. Hardly any one of them agrees with another and which is the correct theory is still a much argued question.

Lamble and Lewis[5] seem to have disproven Arrhenius' theory of "active" and "inactive" molecules, assuming there are such, for we have no proof of it. According to Arrhenius the large temperature coefficient of many reactions is due to the changing of "inactive" into "active" molecules. A catalyst is supposed to act in the same way, causing a shift in this equilibrium. By using a large amount of catalyst the majority of "inactive" molecules would be changed into "active" molecules and then the temperature coefficient should not be so large. But Lamble and Lewis find that the addition of neutral salts causes no change in the temperature coefficient. They offer the suggestion that catalysis is a "radiation" phenomenon. According to this, reactions are catalyzed by the absorption of radiation which the hydrogen ion emits due to its vibration to and fro between two neighboring molecules.

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* A thesis submitted for the degree of Master of Science at Cornell University in June 1926.

[1] Z. physik. Chem., **2**, 194 (1888).
[2] Z. physik. Chem., **4**, 226 (1889).
[3] Z. physik. Chem., **31**, 197 (1899).
[4] Z. physik. Chem., **32**, 348 (1900).
[5] J. Chem. Soc., **105**, 2330 (1900).

Acree[1], who has done considerable work on catalysis says it may be that the changes assumed by Euler play a minor part. He suggests that "reactive" and "less reactive" double salts are formed between the added salt and the reacting substance. These accordingly speed up or slow up the reaction. He also states that changes in solvation, viscosity, vapor pressure, or osmotic pressure also play a part. According to Acree neutral salts change the thermodynamic potential because this depends not only on the substances themselves but also on the surrounding field.

Wilson[2] believes that removal of the solvent by hydration of the salt accounts for the rise in the hydrogen ion concentration. Manning[3] attributes the salt effect to at least two causes acting together. One, which he calls the *true* salt action, is a change brought about by the formation of a new molecular species. $HA + BC \rightarrow HC + BA$. This is accompanied by a readjustment of the concentration of the ions present. The other effect is hydration. He finds that the non-electrolytes, glucose and sucrose, do not increase the rate of hydrolysis of ethyl formate to any appreciable extent. He says: "Therefore . . . it may be concluded that the rate of reaction is independent of changes in concentration of the water. In other words, hydration of the solute does not affect k." He also says that changes in viscosity have little effect and suggests that the acceleration is due to actual changes in the concentration of hydrogen ions in solution. Mannitol[4], a neutral non-electrolyte, and even sucrose itself, will increase the hydrolysis of sucrose.

Taylor[5] says that undissociated molecules of the acid have a catalyzing effect. Åkerlöf[6] believes that the theory of the undissociated molecule having catalytic activity is not correct. He says that the salt molecule does not possess any activity of its own, but is merely the *cause* of the change in the activity of the catalyst. The salt effects a change in the water envelopes surrounding the hydrogen ions. The concentration of the hydrogen ions remains the same while their activity undergoes a change.

Dhar[7] found that the action of neutral salts is highly specific, some accelerating, some retarding the speed of a reaction. Their presence does not alter either the order of the reactions or their temperature coefficients. Rice and Lemkin[8] found that the temperature coefficient was lowered in some cases (by sulphates).

Stieglitz[9] favors the view of Arrhenius that the increase is due to the increased ionization and activity of water. He also says: "The neutral salt effect is due to the fact that we are working with mixed solvents, in which

[1] J. Am. Chem. Soc., **41**, 474 (1919).
[2] J. Am. Chem. Soc., **42**, 715 (1920).
[3] J. Chem. Soc., **119**, 2079 (1921).
[4] Rosanoff and Potter: J. Am. Chem. Soc., **35**, 248 (1913).
[5] J. Am. Chem. Soc., **37**, 531 (1915).
[6] Z. physik. Chem., **98**, 250 (1921).
[7] Z. anorg. allgem. Chem., **128**, 229 (1923).
[8] J. Am. Chem. Soc., **45**, 1896 (1923).
[9] J. Am. Chem. Soc., **34**, 1694 (1912).

ionization, velocities, etc., cannot be expected to be the same as in a pure solvent."

This last suggestion that Stieglitz makes approaches closely the theory which Professor Bancroft suggests and which will be mentioned below. This work was undertaken with the view of testing this theory.

Experimental

The theory that liquid water is a polymerized liquid has been fairly well substantiated[1]. According to this theory liquid water is assumed to be mainly "dihydrol", $(H_2O)_2$. It also assumes that there are other polymers present and that these different forms are all in equilibrium. For example,

$$2\ H_2O \leftrightarrows (H_2O)_2,\ 3\ H_2O \leftrightarrows (H_2O)_3,\ 3\ (H_2O)_2 \leftrightarrows 2\ (H_2O)_3, \text{ etc.}$$

When neutral salts are added to water, they probably cause a shift in this equilibrium[2], giving, at least in some cases, more molecules of "monohydrol", (H_2O). If this is the case we shall have a *different* solvent in which concentrations, reaction velocities, ionization, etc., will be different from those in the original solvent.

With this theory in mind the hydrogen ion concentration in 1/10 normal hydrochloric acid solutions containing one, two, three, and four normal NaCl, NaBr and NaI, was measured with the hydrogen electrode. The effect of these salts on the rates of hydrolysis of sucrose and ethyl acetate was also determined.

Electrometric Measurement of Hydrogen Ion Concentration

For these experiments and all of the following ones, the hydrochloric acid solution was made by redistilling a 20% solution of "C.P." HCl, collecting the middle fraction of the distillate. This was then diluted and standardized carefully. The sodium bromide and sodium chloride were recrystallized and thoroughly dried. The sodium iodide used was Kahlbaum's C.P

Such a quantity of the salt used was introduced into a 50 cc. measuring flask, that when dissolved and diluted to 50 cc. it would give the normality of the salt desired. A quantity of the standardized HCl was added, from a calibrated burette, such that when diluted to 50 cc. it would give 0.1 N HCl. For example, 2.923 gm. of NaCl and 28.62 cc. of 0.17472 N HCl were introduced into the measuring flask and then diluted to 50 cc. This gave a solution one normal with respect to NaCl and 0.1 N with respect to HCl. This solution was then introduced into the hydrogen electrode half of a cell, the other half being a saturated KCl—calomel electrode. The two units were connected in the usual manner[3] by a salt bridge of saturated KCl solution. The E.M.F. of this cell was measured by means of a Leeds and Northrup potentiometer, recording the temperature at which the experiment was made. The hydrogen for the electrode was run from a tank through a hot electric coil to remove the oxygen, and then through a wash-bottle containing dis-

[1] Sutherland: Trans. Faraday Soc., **6**, 105 (1910); Armstrong: Proc. Roy. Soc., **81** A, 80 (1908).

[2] Bancroft: J. Phys. Chem., **30**, 1194 (1926).

[3] Hildebrand: J. Am. Chem. Soc., **35**, 847 (1913).

tilled water. This saturated the hydrogen with water vapor and thus prevented it from changing the concentration of the solution in the cell to any appreciable extent. The cell was always allowed to come to equilibrium before the final measurement was taken. No reading was taken as final until the E. M. F. became constant. The hydrogen electrode was kept in distilled water while not in use, being rinsed off each time with the solution in which it was to be run.

Having measured the E.M.F. of this cell, the apparent hydrogen ion concentration was calculated by means of the following equation:

$$E_{(cell)} = \frac{RT}{nF} \log \frac{1}{(H^{\cdot})} + \text{(value of sat. KCl-calomel electrode against the normal hydrogen electrode at the temperature of the experiment).}$$

where RT/nF was substituted by its value at that temperature along with the conversion factor to Briggsian logarithms.

The E.M.F. of a cell with 0.1 N HCl alone, as the solution in the H electrode, was measured several times, and a constant value was obtained. The salt solutions of 0.1 N HCl were then substituted for the 0.1 N HCl and the E.M.F. of each solution against the calomel measured.

TABLE I

Electrometric Measurement of Hydrogen Ion Concentration.

0.1 N HCl present in each case Normality	E.M.F.	Apparent $H^{\cdot}$ calculated	Percent increase
NaCl			
0	.3080	.096	——
1	.3004	.129	33
2	.2887	.206	114
3	.2783	.310	223
4	.2635	.559	483
NaBr			
0	.3080	.096	——
1	.2990	.140	46
2	.2874	.222	131
3	.2702	.438	357
4	.2551	.800	733
NaI			
0	.3080	.096	——
1	.2900	.192	100
2	.2842	.241	152
3	.2672	.472	391
4	2476	1.020	1062

The liberation of free iodine in the iodide solutions made the results for these somewhat inaccurate. The measurement of the E.M.F. of these solutions was made as soon as possible after making up the solution. In the last column of Table I is given the ratio:

$$\frac{\text{apparent } (H^{\cdot}) - \text{original } (H^{\cdot})}{\text{original } (H^{\cdot})}$$

It can be seen that the apparent hydrogen ion concentration is increased as much as 1000 percent in the case of the four normal sodium iodide solution. It is not likely that the actual hydrogen ion concentration is increased this much. It will now be shown how this increase may be accounted for by the theory mentioned above.

The equation for calculating the hydrogen ion concentration by this method is derived in the following manner:

Nernst's equation for a single electrode potential, Π is $\Pi = RT/NF \log P/p$ where P is the electrolytic solution pressure of the metal (or in this case hydrogen) and p is the osmotic pressure of the hydrogen ions.

If we have two hydrogen electrodes dipping into solutions of different concentrations of H° ions, and eliminate or correct for the difference of potential between the two solutions, the expression for the E.M.F. of this cell is

$$(1) \quad E_{Corr.} = \pi_1 - \pi_2 = \frac{RT}{nF} \log \frac{P_1}{p_1} - \frac{RT}{nF} \log \frac{P_2}{p_2}$$

Then, since we have the same metal (H_2) dipping into two different concentrations of its ions, $P_1 = P_2$ and equation (1) becomes

$$(2) \quad E_{Corr.} = \frac{RT}{nF} \log \frac{p_2}{p_1}$$

In so far as the osmotic pressure is proportional to the concentration we may substitute the ion concentrations c_1 and c_2 for p_1 and p_2. Then

$$(3) \quad E_{Corr.} = \frac{RT}{nF} \log \frac{c_2}{c_1}$$

Now if the solution c_2 is made one normal with respect to hydrogen ions or $c_2 = 1$, equation (3) becomes

$$(4) \quad E = (RT/nF) \log 1/c_1$$

where c_1 is the solution of unknown concentration of hydrogen ions. Knowing the E.M.F. of this cell c_1 could be calculated. However, a hydrogen electrode with a solution one normal with respect to hydrogen ions is difficult to produce, so a saturated calomel electrode is used in place of the normal hydrogen electrode. Since this is about 0.25 volts more positive than the hydrogen electrode, the value of the E.M.F. of this cell is 0.25 more than it would be with the normal hydrogen electrode and equation (4) becomes

$$E = (RT/nF) \log 1/c_1 + 0.25$$

The 0.25 is, of course, substituted by the value the sat. calomel would have against a normal hydrogen electrode at the temperature of the experiment.

It was assumed, in deriving equation (2) that the electrolytic solution pressure (P) of hydrogen was the same in all solutions of its ions. *However*, according to the theory of the shift in the water equilibrium, upon the addition of neutral salts, this is *not* true. We have here a different solvent in which the electrolytic solution pressure is not the same as in water in which neutral salts are not present. Therefore, the equation used to calculate the hydrogen ion concentration would not hold if the electrolytic solution pressure changes. Consequently, the values obtained are not the *true* values of the hydrogen ion concentration, but only the *apparent* hydrogen ion concentrations.

It was thought that the neutral salts, NaCl, NaBr and NaI would affect the equilibrium in the order of Hofmeister's series, i.e. I > Br > Cl. This was found to be true. The bromide gave a greater apparent hydrogen ion concentration than the chloride, and the iodide produced a greater effect than the bromide. This does not agree with the work of Harned[1] who finds that bromides and chlorides have about the same effect on the hydrogen electrode potential. V. A. Arkadiev[2], however, obtained the same relative results that the present work indicates.

Hydrogen Ion Concentration as measured by the Reaction Velocity of Sucrose Inversion.

Since sugar inversion is catalyzed by acid, the rate of inversion can be used as a measure of the hydrogen ion concentration. Experiments were conducted on the increase in the rate of inversion upon addition of the neutral salts used above.

The sugar used in these experiments was of a pure commercial brand that had been dried for two or three days at about 60°C. It was kept in a desiccator over pure concentrated sulphuric acid. The rate of inversion was followed by a Bausch and Lomb saccharimeter. The "normal" solution for this instrument called for 26 gm. sugar per 100 cc. of solution. In these experiments, 6.5 gm. of cane sugar was accurately weighed out each time. This, dissolved and diluted to 50 cc., gave a "half-normal" solution which read "50" on the saccharimeter. The salts and acid were added as before with the exception that the sugar and the salt in the measuring flask were dissolved as much as possible in about 25 cc. of distilled water allowing space enough for the acid to be added. When the acid had been added and the whole diluted to 50 cc. the time was noted. The solution was then placed in a polariscope tube, 20 cm. in length, being careful not to allow any air to remain in the tube when it was closed. The tube was suspended in a thermostat which was regulated at 25°C. ±.05°. Readings were taken on the saccharimeter at different intervals of time and recorded after correcting for the "zero" reading of the instrument. This "zero" reading was taken before and after each reading. The reaction was allowed to continue until a constant reading was obtained. This was taken as the final reading after complete inversion had taken place.

[1] J. Am. Chem. Soc., **37**, 2482 (1915).
[2] Z. physik. Chem., **14**, 192 (1923).

Initial readings had to be taken in each case with the desired concentration of sugar and salt present, because it was found that the salts decreased the rotation of the sugar. The algebraic sum of the initial and final readings gave the total change. The percent sugar present at the time t was found as follows:

$$\% \text{ Sugar} = \frac{\text{reading at time } t - \text{final reading}}{\text{total change in readings}} \times 100$$

The reaction velocity constant was calculated by the following equation, using percent to express concentrations,

$$.4343\ k = 1/t \log_{10} \frac{100}{\% \text{ Sugar}}$$

The results which are given in Table III are the means of a series of values of k of which the data in Table II are typical.

TABLE II

Sugar Inversion with 0.1 N HCl and 2 N NaCl

Time in hours	% Sugar	k	Mean
1	89.1	.1151	
2	79.4	.1151	
3	70.8	.1150	
4	62.7	.1165	
5	56.1	.1155	
6	49.4	.1171	.1158
8	39.4	.1164	
9	35.1	.1163	
10	31.5	.1154	
11	27.7	.1166	
12	25.1	.1151	

TABLE III

Effect of Neutral Salts on the Inversion of Cane Sugar
(in the presence of 0.1 N HCl)

Normality of Salt	k	Percent increase in value of k	Percent increase in apparent H·
	NaCl solutions		
0	.0514	—	—
1	.0798	55	33
2	.1158	125	114
3	.1714 (approx.)	233	223
4	.2950	473	483
	NaBr solutions		
0	.0514	—	—
1	.0852	65	46
2	.1441	180	131
3	.2312	349	357
4	.3700 (approx.)	620	733

In the cases of 3 N NaCl and 4 N NaBr the constant obtained was not satisfactory so these values are only approximate. The iodide solutions could not be followed on a saccharimeter because the solution became so colored that sufficient light did not come through the solution to obtain an accurate reading.

Upon comparison of the results obtained by the two methods it is seen, that the percentage increase, for the same normality of salt, in the reaction velocity agrees, within the limits of experimental error, with the percentage increase as given by the electrometric method. The percentage increase as given by the 4N bromides does not agree very well but the value of k for this concentration of salt in the sugar inversion is only approximate.

Hydrolysis of Ethyl Acetate

On examining the literature[1], it was found that the results obtained by the hydrolysis of ethyl acetate did not agree with those obtained by the inversion of sugar, in the case of sodium chloride. Åkerlöf's experiments were then repeated, using 0.1 N hydrochloric acid instead of 0.05 N. This concentration (0.1 N) was the concentration of HCl used in the former experiments. The reaction velocity of the hydrolysis of salt-free 0.05 molar ethyl acetate in the presence of 0.1 N HCl was determined. Then the reaction velocity of the same mixture with the addition of two and four normal sodium chloride was measured.

The ethyl acetate used was Kahlbaum's C.P. It was purified by washing three times with a 5% solution of sodium carbonate and then dried for two days over calcium chloride. It was then redistilled, a constant-boiling product being obtained. Only the middle fraction of the distillate was collected. The ethyl acetate was placed in a tightly-stoppered bottle which was then kept in the thermostat. The stock bottle of the acid and the measuring flask containing the salt in solution were kept in the thermostat so that all the solutions were at the same temperature when mixed. In all the experiments, with the exception of the last one, one cc. of pure ethyl acetate was added to the salt and acid solution and the whole diluted to 200 cc. giving 0.05 molar ethyl acetate and 0.1 N HCl. 10 cc. samples were withdrawn at intervals and run into 10 cc. of sodium acetate solution (0.5 N) to stop the reaction. The excess acetic acid formed and the HCl present were titrated with CO_2-free sodium hydroxide, using phenolphthalein as an indicator. The samples were withdrawn by means of a special pipette arrangement consisting of a 10 cc. pipette sealed on to a capillary stop-cock (two-way). This was sealed on the single-arm side of the stopcock. One of the other arms dipped into the solution in the reaction mixture through a tightly-fitting rubber stopper. The third arm was drawn out into a tip close to the stop-cock and was used as the delivery tube. The beginning titre was taken in each case with the desired amount of salt present in the acid. These samples were also titrated in the presence of the 10 cc. of 0.5 N sodium acetate. The end-point of the reaction was found by sealing some of the solution in a tube and heating in a

[1] Åkerlöf: Z. physik. Chem., 98, 260 (1921).

water bath at about 75°C. for 12 hours. The tube was then placed in the thermostat and allowed to cool for the same length of time. The velocity constant, k, was found by the following equation:

$$.4343\ k = 1/t \log_{10} \frac{A - x_o.}{A - x_t}$$

where A = end titer in cc. of NaOH, x_o = titer when the time t = o, x_t = titer at time t, and t = time in hours. The data are given in Table IV.

TABLE IV

Effect of NaCl on the Rate of Hydrolysis of 0.05 M Ethyl Acetate in the Presence of 0.1 N HCl.

Time in Hours	cc. NaOH	k	Mean	% Increase
Salt-free Solution				
0	11.30			
2	11.80	.0435		
3.5	12.10	.0411		
5	12.44	.0425	.0417	—
7.5	12.90	.0416		
8	12.93	.0400		
Infinite	17.25			
2 N NaCl				
0	11.35			
2	12.05	.0544		
4	12.61	.0599		
5	12.90	.0609		
6	13.11	.0590	.0595	42 (Åkerlöf 46%)
7	13.35	.0591		
8	13.70	.0634		
Infinite	17.25			
4 N NaCl				
0	11.35			
1	11.90	.0962		
2.5	12.52	.0872		
3	12.78	.0915		
4	13.04	.0834		
5.5	13.62	.0872	.0885	112 (Åkerlöf 98%)
6	13.81	.0884		
7	14.10	.0885		
8	14.33	.0868		
9	14.60	.0877		
Infinite	17.35			

These results are approximately the same as Åkerlöf's so it is to be concluded that this reaction is affected differently by the change in solvent, the

reaction velocity of this hydrolysis not being increased as much as in the case of sugar inversion. This is to be expected because we are dealing with different chemical substances and it is not likely that these would be affected the same by a change in the solvent.

On conducting some experiments on the effect of bromides on this reaction, Table V, it was found that they did not give as much increase in the reaction velocity as the chlorides. This should not be the case. If the bromides gave more of an increase in the one reaction, they ought to in all reactions, unless some other complicating factor enters into the reaction[1].

The experiments on the two normal sodium chloride and sodium bromide solutions were then repeated. Checks were obtained in the case of the chloride. The bromide gave a still lower value of k than the first trial. An average of these two was taken as the correct value.

TABLE V

Effect of NaBr on the Rate of Hydrolysis of 0.05 M Ethyl Acetate in the Presence of 0.1 N HCl.

Time in Hours	k	Mean	% Increase Bromide	% Increase Chloride
	2 N NaBr			
1st trial	.0557	.0541	29	42
2nd trial	.0525			
	4 N NaBr			
1	.0732			
1.5	.0713			
2	.0724			
3	.0673			
4	.0703	.0709	70	112
6	.0683			
7	.0717			
8	.0707			
8.5	.0730			

Poma[2] agrees with these results in his study of the hydrolysis of ethyl acetate. He finds that the accelerating influence decreases in the order Cl, Br, NO_3, I.

It is evident that in the case of the bromides some substance in the reaction mixture was affecting the acid or the salt so that their accelerating influence was decreased. To find the disturbing factor the reaction was run with 1st 0.1 molar ethyl alcohol, 2nd 0.1 acetic acid present in the reaction mixture from the start. Both of these are products of the reaction. The data are given in Table VI.

[1] Iodides increase the solubility of ethyl acetate in water, according to Glasstone and Pound: J. Chem. Soc., **127**, 2660 (1925).

[2] Gazz., **41** I, 353 (1911).

TABLE VI

Effect of Ethyl Alcohol and Acetic Acid on the Rate of Hydrolysis of 0.05 M Ethyl Acetate in the Presence of 2 N NaBr and 0.1 N HCl.

Time in Hours	k	Mean	% Increase
	0.1 M Ethyl Alcohol (approx.)		
1	.0449		
1.5	.0513		
2.5	.0562		
3	.0582		
4	.0536	.0549	31
5.5	.0581		
6.5	.0582		
7	.0594		
	0.1 N Acetic Acid (approx.)		
1.5	.0525		
3	.0579		
3.5	.0551		
4	.0577		
5.5	.0564	.0564	35
6	.0557		
6.5	.0563		
7	.0566		
7.5	.0597		

It can be seen that the addition of alcohol or acetic acid had little or no effect on the reaction velocity. However, it was noticed that the value of k obtained in all the reactions with bromides was not constant, but rose steadily, with a few exceptions, as the reaction proceeded. From this it is apparent that it must be the ethyl acetate which is affecting the reaction. For, as it decreases, due to reacting with the water, its inhibiting effect decreases, and the reaction velocity increases. An experiment was then made with 0.1 molar ethyl acetate instead of 0.05 molar. The mean value of k, for the length of time the other experiments were run, was 0.0511 or only a 22% increase. If it was the ethyl acetate that was slowing up the reaction, as this last experiment seems to indicate, the value of k ought to increase until, as the time approaches infinity, it reaches at least the value of k obtained with the chlorides. The reaction was then continued, taking readings up to 32 hours, Table VII.

As seen by Table VII, the value of k did increase, by that time, to the value obtained with the chloride, i.e. .0590. This value of k would probably continue to rise, for 32 hours does not represent infinity. The titre in cc. of NaOH had increased in 11 hours after the reading at 32 hours only from 19.6 to 20.48. The final end-point titre was 21.2 cc. and this was not reache until several hours later.

TABLE VII

Hydrolysis of 0.1 Molar Ethyl Acetate in the Presence of 2 N NaBr and 0.1 N HCl.

Time in Hours	k	Time in Hours	k
1.5	.0482	13	.0547
2	.0499	14	.0549
2.5	.0510	16	.0549
3	.0517	19	.0552
3.5	.0516	21	.0561
6.5	.0519	22	.0558
7	.0522	23	.0566
8	.0523	26	.0576
9	.0559	28	.0578
10	.0559	30	.0585
11	.0537	32	.0590
12	.0558		

Mean of first 8 = .0511 = 22% increase

The work of Glasstone and Pound[1] on the effect of salts on the solubility of ethyl acetate in water indicates that bromides do not decrease the solubility of ethyl acetate in water as much as chlorides, and iodides less than bromides. In fact, lithium bromide and iodide *increase* the solubility of ethyl acetate in water till, with the 60% lithium iodide, ethyl acetate and water are miscible in all proportions! In general, bromides and iodides are more soluble in ethyl acetate than are chlorides. These two effects would tend to prevent bromides from having as much effect on the reaction velocity as chlorides.

This work was undertaken at the suggestion of Professor W. D. Bancroft, and carried out under his direction. To him the writer wishes to express his sincere appreciation.

The writer also wishes to thank Dr. G. H. Brandes for his aid in the electrometric measurements.

Cornell University

[1] J. Chem. Soc., **127**, 2660 (1925).

NEW BOOKS

Science Religion and Reality. *Edited by Joseph Needham. 22 × 15 cm; pp. 396. New York: The Macmillan Company, 1925. Price: $2.50.* The book opens with an introduction by Lord Balfour and closes with a conclusion by Dean Inge. In between are articles entitled: Magic Science and Religion, by Bronislaw Malinowski; Historical Relations of Religion and Science, by Charles Singer; Science and Religion in the Nineteenth Century, by Antonio Aliotta; The Domain of Physical Science, by Arthur Eddington; Mechanistic Biology and the Religious Consciousness, by Joseph Needham. The Sphere of Religion, by John W. Oman; Religion and Psychology, by William Brown; Science Christianity and Modern Civilisation, by Clement C. J. Webb. Some of us would like more commas; but the omissions seem intentional.

"The conception of a material universe, overwhelming in its complexity and its splendour, yet potentially susceptible of complete explanation by the actions and reactions of two very minute and simple kinds of electrical sub-atom, is, without doubt, extraordinarily fascinating. From the early days of scientific philosophy or (if you prefer it) of philosophical science, thinkers have been hungering after some form of all-embracing atomism. They have now apparently reached it (so far as matter is concerned) by the way of observation and experiment—truly a marvellous performance. Yet the very lucidity of the new conceptions helps to bring home to us their essential insufficiency as a theory of the universe. They may be capable of explaining the constitution and behaviour of inanimate objects. They may go some (as yet unmeasured) distance towards explaining organic life. But they certainly cannot explain mind. No man really supposes that he personally is nothing more than a changing group of electrical charges, so distributed that their relative motions enable or compel them in their collective capacity to will, to hope, to love, to think, perhaps to discuss themselves as a physical multiplicity, certainly to treat themselves as a mental unity. No creed of this kind can ever be extracted by valid reasoning from the sort of data which the physics either of the present or the future can possibly supply," p. 14 (Balfour).

"When we examine the literary monuments of the classical culture—of which we are the heirs and the Greeks the earlier and main intellectual representatives—we cannot fail to be impressed by the vastness of its interests, the enormous mental energy that it displays and the bulk and completeness of its remains. Considering these things the comparative backwardness of the religious development of that culture is a very striking feature. Greek religion—using that word in the restricted sense—never reached the rational standard of the Hebrew religion. Thus no complete and worked-out Greek cosmology, incorporated in a religious atmosphere, has come down to us. The popular Greek religion, in fact, never reached the coherent level of the Hebrew, or reached it only in later times and then in competition with philosophical or other systems which themselves made religious claims, and notably in contact with Christianity. . . .

"The absence of a sacred Canon and the relatively low grade of their religion is in contrast to their scientific and philosophical development for which, as some think, way was thus made. At a remarkably early stage in their development the Greeks observed not only that their world was subject to laws, but that by investigation these laws are ever further and further discoverable. A belief in such natural laws plays no part in the more ancient Hebrew scriptures, which, moreover, contain very little of that curiosity which is the parent of science. It was with the Ionian Greeks that the scientific idea was born, and it can be traced back among them with some clearness to the sixth century B. C.," p. 91 (Singer).

"It was thus not the *practice* of science which the Greeks invented, but the *scientific idea*, the conception that the world was knowable inasmuch and in so far as it could be investigated. In ancient times this idea led to a special point of view and to some amelioration of man's lot. In modern times it has led to a complete transformation of our mode of life, to a profound modification of the interrelations of peoples, and to an alteration in our

attitude to each other and to the world around us. It would be idle to pretend that these changes have been entirely to the good. We believe, however, that an impartial survey of the general effects of the scientific idea upon men's minds and hearts throughout the ages will result in an overwhelming verdict in its favour as a very beneficient and humanising instrument. In helping man to gain a clear idea of the knowable world, science has also helped him to understand his fellow-man," p. 92 (Singer).

"The physical philosophers of the fourth century, of whom Aristotle is the greatest and most permanent type, were more successful than Plato in their efforts at constructing a coherent and lasting cosmic theory. We may glance at the picture of the material universe presented by Aristotle. That great thinker was himself an absolutely first-class naturalist. Thus the cosmic scheme that he produced, unlike that of Plato, absorbed a vast mass of observational material, notably in the department of biology. Yet the bases of the scheme were certain preconceived notions which did not and could not depend upon observation. Into this scheme observations had to be fitted. The difficulty of fitting them represents a struggle between the observational and theoretical interests which is a prototype of that so often encountered in later centuries," p. 101 (Singer).

"Despite the spread of philosophy based on science, the observational activity of antiquity was slowly dying from about 100 B. C. In A. D. 200 it expired with Galen. The decay of observation, as we have seen, was the result of internally acting causes. In origin it had nothing to do with Christianity, which was not yet in a position to have its full effect on pagan thought.

"But Christianity did come as a protest and a revulsion against the prevailing and extremely pessimistic outlook. Men had lost interest in the world and Christianity brought them something to live for, it brought a *cause*. It was natural under these circumstances that Christian thought should oppose the philosophical basis of pagan thought. In this sense early Christian thought was certainly anti-scientific and exhibits an aversion to the view which places the whole of man's fate under the dominion, the inescapable tyranny, of natural law. It is, however, essential to remember that the Early Church in developing this opposition was not dealing with living observational science. The conflict was simply with a philosophical tradition which contained dead, non-progressive, and misunderstood scientific elements. The conflict in the Early Church, therefore, though exceedingly interesting in itself, is of little importance for our subject and we can afford to pass it by.

"As the centuries wear on and as Christianity becomes more firmly established as the state religion, the need for a coherent philosophical system becomes more pressing. During the earlier Middle Ages this need is met on the scientific side largely by that bizarre work of Plato, the "*Timaeus*." As time goes on Aristotelian elements become more and more prominent, and by the thirteenth century these Aristotelian elements occupy the main field. The great system of Catholic philosophy, of which St. Thomas Aquinas was the leading architect, was built upon the recovered writings of Aristotle. The work of Aquinas is merely the greatest and most lucid effort of a process that had been going on for centuries. His "*Summa Theologica*," regarded as a sustained intellectual effort, must be considered one of the most remarkable and fatiguing performances that the human race has yet achieved. As an investigation of evidence for the views that it sets forth, the modern working scientist will pass it by," p. 114 (Singer).

"But it may be asked, was there then no science in the Middle Ages? Were none of the heresies, for instance, with which the Church had to deal of the nature of scientific hypotheses? To answer this question is difficult, and yet we must attempt it. To answer it with completeness we should have to define what we mean by science and this would lead us far afield. We may note, however, that science in its most developed form exhibits certain characteristic features.

"(*a*) It deals with judgments to which universal assent is obtainable.

"(*b*) It is a consciously progressively increasing body of knowledge and doctrine.

"(*c*) The only tests of validity that it can accept are the tests of experience, and these tests it must always demand.

"(*d*) An essential process of science is the drawing up of general laws from the results of observation.

"(*e*) It is necessary for the growth of science and is perhaps a corollary of the other features that the conclusions, being based on the evidence, should not be prejudged.

"Now a fixed and definite scheme of the Universe was accepted as a postulate by all thinkers of the Middle Ages. That scheme was derived from Aristotle but modified to fit the specific Christian doctrine of creation. With these things always before the mind, scientific investigation in our sense of the word was almost impossible to the medieval man. He could never embark on that great voyage of exploration with the sense of infinite possibilities which is the birthright of every young researcher nowadays," p. 117 (Singer).

"During the thirteenth century there was much interest in optics; the attention devoted to the subject led in about the year 1300 to the application of lenses—which had been known to the Arabian writers—as spectacles. A similar process had led at an even earlier date to the adaptation of the magnet to the mariner's compass. These are discoveries of first-rate importance and we cannot pass them by in silence. But—and this is where we sense the characteristic medieval atmosphere—*these discoveries led to the production of no general laws*. The lens led to no advance in the doctrine of refraction or in the theory of light. The compass revealed nothing of the nature of terrestrial magnestim to the medieval thinker. They were on the level of *inventions* rather than definite steps in scientific progress. The actual application of these discoveries was far more important to the men of the time than were the principles involved. If we seek for interest in the eliciting of new general laws of nature we shall have a long and fruitless hunt in the vast wilderness of time that we call the Middle Ages," p. 119 (Singer).

"The Inquisition as a separate, regular, and legally established method of establishing faith and uprooting error makes its appearance in the thirteenth century. Our horror at its methods, our indignation at its injustice, our detestation of its blood-stained and infamous history, must not mislead us into regarding it as an attack on the experimental method, or as a means of suppressing at its birth a monster which if allowed to live and grow would one day strangle religion. There can be no reasonable doubt that in the sixteenth, seventeenth, and eighteenth centuries the activities of the officers of the Inquisition were directed to the suppression of scientific views that were held to be dangerous to the faith. In the centuries that preceded, however, no such tendency can be distinguished. The reasons for this are simple. During those earlier centuries, on the one hand experimental methods produced no conclusions that were dangerous to current theology, and on the other it is extremely unlikely that any officer of the Inquisition ever grasped the nature of the scientific method. So far as the Middle Ages are concerned we can therefore put aside the Inquisition as irrelevant to our discussion," p. 121 (Singer).

"To us who live only a generation or two after the disturbances of the spirit caused by the Evolution controversy, it may seem that biological rather than physical science is the department likely to clash with the claims of traditional religion. Yet historically this is not the case. The successors of Vesalius continued to prosecute their studies until the nineteenth century unnoticed or even directly aided by the Churches. It was the cosmical speculations of the astronomers and physicists, not the investigations of the biologists, that attracted unwelcome ecclesiastical attention," p. 129 (Singer).

"Historically men of science have found various modes of escape from the tyranny of determination. The majority of men of science, like the majority of other men, have small philosophical powers. They, like most other men, have accepted their religion as they have found it. They have made their science their daily occupation without clear relation to their religious convictions. A proportion of scientific men, incensed by the mere discrepancy between the biblical and the scientific record, have abandoned more or less completely their relation to religion. A considerable section of these have ranged themselves as 'agnostic.' Yet there remain two religious points of view that can never be affected by any extension of the scientific realm. The one would completely separate internal experience from external experience. The man who does that is safe; he has fled, as have many before him, to a haven of peace down the mystic way. The second would regard man's soul not alto-

gether as his own possession, but as part of a great world-soul. This combination of determination and pantheism is a refuge, not infrequently sought in antiquity, to which many a student of science has turned in modern times, from the days of Spinoza onward," p. 148 (Singer).

"The confession of impotence by agnostic naturalism led, towards the end of the century, to a return to the romantic spirit of the beginning of the century. Science, of which Positivism had been the first to proclaim the apotheosis, was submitted to criticism, and revealed the abstraction of its concepts and of its theories, which do not make us gather the reality of its living richness, but only the skeleton of it. It was found that those theories are also at bottom a human construction, variable and relative, and that they suppose an act of faith at their roots. In this way the distinction between pure reason and practical reason which Kant had made was shown to be artificial, because the activity of the scientists is itself directed to a practical end; that is, to that of dominating nature, of finding suitable schemes which may serve to guide us through the complexity of the phenomena of experience. Thus religion and science were reconciled in their common origin, which is always an act of free will, a free adhesion of the spirit; and dualism was superseded.

"According to Pragmatism, of which William James and F. C. S. Schiller are the most illustrious representatives, the sole function of science is to serve for action, to provide us with methods to follow in order that we may see this or that phenomenon appear, or in order that we may obtain this or that result. A proposition which does not generate practical results has no meaning. Two propositions which bring no result in their manner of acting differ only verbally. According to the Pragmatist, there is no truth which must be reflected from without, or to which the thought must correspond to be called true. Truth and reality are constructed actively by ourselves. There exists no perfect system laid down *ab aeterno*, with immutable laws; but reality is always on the road towards being made, a ceaseless creation, in which we collaborate with our energetic forces," p. 166 (Aliotta).

"The learned physicist and the man in the street were standing together on the threshold about to enter a room.

"The man in the street moved forward without trouble, planted his foot on a solid unyielding plank at rest before him, and entered.

"The physicist was faced with an intricate problem. To make any movement he must shove against the atmosphere, which presses with a force of fourteen pounds on every square inch of his body. He must land on a plank travelling at twenty miles a second round the sun—a fraction of a second earlier or later the plank would be miles away from the chosen spot. He must do this whilst hanging from a round planet head outward into space, and with a wind of ether blowing at no one knows how many miles a second through every interstice of his body. He reflects too that the plank is not what it appears to be—a continuous support for his weight. The plank is mostly emptiness; very sparsely scattered in that emptiness are myriads of electric charges dashing about at great speeds but occupying at any moment less than a billionth part of the volume which the plank seems to fill continuously. It is like stepping on a swarm of flies. Will he not slip through? No, if he makes the venture, he falls for an instant till an electron hits him and gives a boost up again; he falls again, and is knocked upwards by another electron; and so on. The net result is that he neither slips through the swarm nor is bombarded up to the ceiling, but is kept about steady in this shuttlecock fashion. Or rather, it is not certain but highly probable that he remains steady; and if, unfortunately, he should sink through the floor or hit the ceiling, the occurrence would not be a violation of the laws of nature but a rare coincidence.

"By careful calculation of these and other conditions the physicist may reach a solution of the problem of entering a room; and, if he is fortunate enough to avoid mathematical blunders, he will prove satisfactorily that the feat can be accomplished in the manner already adopted by his ignorant companion. Happily even a learned physicist has usually some sense of proportion; and it is probable that for this occasion he put out of mind scientific truths about astronomical motions, the constitution of planks, and the laws of probability, and was content to follow the same crude conception of his task that presented itself to the mind of his unscientific colleague," p. 189 (Eddington).

"The central point of Einstein's great theory is a new law of gravitation approximating to but more accurate than Newton's law, and we shall start by explaining exactly the formulation of this law. Our explanation will be more thorough than usual, for we shall make a point of defining each new term that it is necessary to introduce. Probably the effect of giving so full an explanation will be that the reader will not understand the new law any better at the end than he did at the beginning. That does not matter. He is asked to keep his attention fixed on the form of the explanation rather than on the substance of the explanation; we want to indicate to him the train of ideas that he would have to exhaust if he wished to get to the bottom of the significance of the new law.

"Einstein's law of gravitation is a statement that in empty space ten quantities called *potentials* satisfy certain rather lengthy mathematical equations which can be exactly specified. (The term "potential" will be explained presently.) In other words, whereas we might conceive a world in which the potentials at every moment and at every place had entirely arbitrary values, the actual world around us is not so unlimited. The statement that actual phenomena are more limited in variety than imaginable phenomena is evidently equivalent to the statement that the actual world is governed by a law. The next question is, What are the "potentials" which are governed by the law that has been specified? They are derived by simple mathematical calculations from certain other quantities called *intervals*. If we know the values of the various intervals through the world we can at once find the potentials. What are these "intervals"? They are relations between pairs of events which are measured by the *scale* or *clock*. Instructions can be given describing exactly how the scale and clock are to be employed, and the interval is merely the scale-reading or clock-reading or a particular combination of the two readings. Next question, What are "scales" and "clocks"? It would take a somewhat long description to prescribe exactly what constitutes a perfect scale or clock referred to here, but with patience all the requirements can be stated; we should, however, find it necessary to introduce a new word which ought to be carefully explained—the scales and clocks are made of *matter*. Next question, What is "matter"? That has often been asked, with many diverse answers; but here the answer is not so difficult. Metaphysical properties of substantiality have no bearing on the efficiency of a clock as an instrument of measurement, it is only the mechanical properties of matter which concern us here; and, so far as mechanics is concerned, matter is merely the embodiment of three measurable entities, *mass*, *momentum*, and *stress*. What are "mass," "momentum," and "stress"? It is one of the remarkable (though comparatively little known) achievements of Einstein's theory that it has succeeded in describing exactly what these are. They are certain analytical expressions containing various combinations of the *potentials*. What are the "potentials"? Why, that is just what I have been explaining to you!

"The definitions of physics proceed according to the method immortalised in "The House that Jack Built": *This is the potential, that was derived from the interval, that was measured by the scale, that was made from the matter, that embodied the mass.* . . . But instead of arriving ultimately at "Jack," whom, of course, everybody knows without need of introduction, we make a circuit back to the beginning of the rhyme . . . "that killed the rat, that ate the malt, that lay in the house—that was built by the priest all shaven and shorn, that married. . . ." So now we can go around and round for ever," p. 203 (Eddington).

"Actuality is recognised as tremendously important by the experimental physicist. But it does not appear in the scheme of the theoretical physicist. And it is quite natural that it should not appear. The experimental physicist deals with the particular cases; the theoretical physicist generalises; he refines away that which is special and particular and seeks to obtain the general laws of nature. So that he eliminates the reference to one particular and actual world and arrives at a theory which applies to all possible conditions that might occur—this, of course, includes the actual world as a special case. The theoretical physicist thus necessarily excludes actuality from his purview, though he arranges that it can be added as an afterthought; and we can see how admirably the device of the

vicious circle of definition is adapted to this purpose, because if actuality is added at any point it runs throughout the whole cycle. If our potentials are actual, then our matter, clocks, scales, intervals, etc., will all become actual.

"Theoretical physics leaves room for actuality to be added, but it cannot itself tackle the question. It makes no attempt to define actuality. The experimental physicist, for whom actuality is vitally important, has to turn elsewhere, and he turns to consciousness. He simply accepts as actual that which the mind recognises as actual. He is alert for criticism of the reliability of his scales and clocks, but he has no misgivings as to their actuality. It is, of course, not necessary to appeal to the mind in each particular instance; when once actuality has been introduced at any point of the cycle it runs through the whole cycle. But to obtain a start we must be given something certified as actual by the mind," p. 210 (Eddington).

"Some reference must be made to the time-long difficulty of understanding how a man can voluntarily produce or refrain from producing effects in the physical world without (so experiment teaches) setting aside any of the laws known to govern inorganic nature. The difficulty is undoubtedly a grave one, and we cannot offer a solution of it; but it is somewhat modified by the newer conception of the nature of the laws governing the physical world. In the present stage of science the laws of physics appear to be divisible into three classes—the identical, the statistical, and the transcendental. The 'identical laws' include the great field-laws which are commonly quoted as typical instances of natural law—the law of gravitation, the law of conservation of mass and energy, the laws of electric and magnetic force, and the conservation of electric charge. These are seen to be identities, when we refer to the cycle so as to understand the constitution of the entities obeying them; and unless we have misunderstood this constitution, violation of these laws is inconceivable. They do not in any way limit the actual basal structure of the world, and are not laws of governance. To quote again from Professor Weyl, "The freedom of action in the world is no more restricted by the rigorous laws of field physics than it is by the laws of Euclidean geometry according to the usual view." You have unfettered freedom to draw anything you like on a flat sheet of paper; all the same, you cannot draw a circle whose circumference is six times its diameter. But you would not complain that because of this inability to do impossible things your freedom is imperfect. The law of Euclidean geometry is not felt to be a restriction on the freedom of the artist; similarly the law of gravitation, when the nature of that which obeys it is understood, cannot be regarded as a limitation of freedom. The 'statistical law,' including the laws of gases and thermodynamics, are the laws obeyed by crowds independently of the characteristics of the individuals composing the crowds. There remain the 'transcendental laws,' namely, the laws of atomic structure and of the quantum theory, which so far as we know may be true laws of governance. The quantum theory, perhaps even more than the relativity theory, is a remarkable development of the last twenty years, constituting an amazing breach with the traditional type of physical theory. It includes certain precise laws confirmed by innumerable experiments in all branches of physics, but no one has succeeded in forming an intelligible conception of the quantum processes. One thing is generally accepted, that we have here entered a domain of law of a type to which our experience of the great laws belonging to the first class gives no clue.

"Interference of human free will with the identical laws cannot be admitted; even omnipotence could scarcely set these aside, and free will does not mean omnipotence. It must be statistical or transcendental laws that are modified when we "make up our minds" to do something. It would be a comfortable theory if we could lay the whole blame of free will on the transcendental laws—particularly on those which have not yet been discovered! But I fear that there can be no satisfactory theory of free will without admitting an interference with statistical laws. If a human being can produce motion of material objects as the result of a mental resolution—motion which would not have resulted from the automatic interplay of electrons and atoms in his brain and body—it seems clear that those electrons and atoms are for the time not behaving as an ungoverned swarm would do, and some at least of the statistical laws governing random crowds will fail to hold. Indeed, the mind

must necessarily have its grip on the crowd rather than on the individual atom or quantum-process, for the contact of matter and spirit is between brain and mind and not between an atom of brain and a (conjectural) atom of mind. If the physical aspects of what is occurring conform to statistical laws, the mental resolution itself must be governed by statistical laws, and is therefore not what it appears to be—a simple decision of will—but a conflict of billions of unrecognised mental elements.

"The serious difficulty arises that at present no failure of the statistical laws has been detected in experiments made on living organisms, and that the chief of these laws—the second law of thermodynamics—has been verified with some accuracy. Whilst this difficulty is perhaps not insuperable, it must not be minimised," p. 214 (Eddington).

"It is usually considered in this present age of universal specialisation that the business of men is to speak only about their own affairs, and, if they have any world-outlook, to keep it to themselves. Particularly is this the case with the scientific worker; but he is not alone in his mental prison. There adjoins it another, equally commodious but equally well bolted from outside, which is inhabited by the theologian and the mystic. In fact, there is a whole honeycomb of cells, each containing a section or two of human thought and experience, and the prison is so constructed that whatever opinions the inmates may have about each other, whenever they happen to open their mouths thereon they are miraculously struck dumb," p. 221 (Needham).

"The ever-rising tide of specialisation has obscured the fact that there are not a few problems, especially in the fields of pure knowledge, which cannot be understood in the terms of one subject. The spectrum of knowledge has been arbitrarily divided up into compartments, whereas the colours really shade into each other quite imperceptibly. Such arbitrary cuttings and slicings have often mutilated the delicate fabric of reality, with the result that there are many questions at the present time most urgently needing the synthesis of two or more illuminations. As an example we might adduce our knowledge of the nervous system of man. It has been studied from three main directions: experimental psychology has examined it, biochemistry has studied its metabolism and its chemical composition, and biophysics has collected data about its electrical phenomena. But no one has yet synthesised these items of knowledge into one unitary whole," p. 222 (Needham).

"Physiology, which had had little to say to the evolution theory, since taxonomic classification had been founded on differences of form rather than of function, now began to occupy more and more the centre of the field, and as this process went on it was seen that physiology wore no longer the garments in which traditional teaching had pictured her, but appeared in the breast-plate of chemistry, the helmet of physics, and armed with the spear of mathematics. As time went on the hitherto neglected subject of biochemistry became more and more important, so that at the present day zoology has become comparative biochemistry and physiology biophysics. The causes for the change lie deep, but the effect has been profound infiltration of physico-chemical ideas and terminology into the whole biological field, and this implies a corresponding peaceful penetration of the mechanistic theory of life. This change from comparative morphology to comparative biochemistry is indeed one of the most important factors in the scientific history of the last few decades. It will never again be equalled in importance until comparative biochemistry passes over into electronic biophysics. For it means that we have passed one step deeper into the problem of life—important as the distribution and form of organisms may be, it cannot be so much so as the actual examination of the physico-chemical attributes of living matter itself, of the universal substrate of the innumerable manifestations of living beings. The forms of the different types of sea-urchins are truly most interesting, but they are only the form taken by the same chemical elements, and in this case as in others the body is more than the raiment," p. 224 (Needham).

"At the present day then the situation is in effect the complete triumph of mechanistic biology. It is not alone in the field, because the neo-vitalists do exist as a small minority, but the vast preponderance of active biological workers are mechanists. We have already given four instances of the antagonism between theology and mechanistic biology, and we can now add a fifth. At the Modernist Conference held at Oxford in the summer of 1924

all the speakers on biological subjects were professed and eminent vitalists. Nothing could be more beautifully in line with the traditional manner. But although it is possible to understand the alacrity with which the theological mind greets vitalistic and spiritualistic ideas in biology, yet it may be doubted whether, even from a narrowly apologetic point of view, it was wise to nail the colours of religion to the precarious mast of neo-vitalism," p. 235 (Needham).

Wilder D. Bancroft

The Hydrous Oxides. *By Harry B. Weiser. 21 × 14 cm; pp. x + 452 New York and London: McGraw-Hill Book Company, 1926. Price: $5.00.* In the preface the author says: "No group of substances presents a greater variety of colloidal properties than the hydrous oxides. For this reason they have been employed frequently in the investigation of colloid chemical phenomena and applied in widely diversified ways to the industrial arts. There is little doubt that a more intimate acquaintanceship with this group of substances will serve to extend their field of usefulness rapidly. It is hoped, therefore, that the book may prove of value alike to scientist and industrialist." The subject is treated under the general heads: jellies and gelatinous precipitates; the hydrous oxides of iron; hydrous chromic oxide; the hydrous oxides of aluminum, gallium, indium, and thallium; the hydrous oxides of copper, cobalt, nickel, silver, and gold; the hydrous oxides of beryllium, magnesium, zinc, cadmium, and mercury; the hydrous oxides of silicon and germanium; the hydrous oxides of tin and lead; the hydrous oxides of titanium, zirconium, and thorium; the hydrous oxides of the rare earths; the hydrous oxides of the fifth group; the hydrous oxides of molybdenum, tungsten, and uranium; the hydrous oxides of manganese; the hydrous oxides of the platinum family; tanning; mordants; water purification; cement; the soil.

It is interesting to note that a century ago Rose observed that glycerol, mannite, sucrose, and glucose will prevent the precipitation of hydrous ferric oxide on adding of alkali or ammonia to a solution of a ferric salt. A small amount of hydrous ferric oxide inhibits the crystallization of cane sugar to such an extent that a high percentage of molasses is obtained in plant work if the raw sugar is kept in iron vessels or if the clearing 'char' contains iron, p. 44. Wintgen calculates that one micelle of aged iron oxide sol is balanced electrically by over ten thousand chlorine ions, p. 51.

"The adsorbability of the alkalies deduced from their power to cut down the adsorption of barium ion is in the order : K > Na > Li. From the curves in Fig. 7 it will be seen that the precipitation value of barium chloride is increased by like amounts of alkali chlorides in the order LiCl > NaCl > KCl; while in the presence of HCl, the precipitation value of barium salt first rises to a point just below that in the presence of a like amount of lithium chloride and then drops off rather sharply. The following explanation of these phenomena is suggested: For a given alkali chloride concentration, precipitation will take place when the combined adsorption of the two cations neutralizes the combined adsorption of chloride and hydrosulfide ions. The combined adsorption will be equivalent for different pairs of cations; but the relative amounts of each that make up this equivalent adsorption will vary, depending as it does on the relative adsorbability of the two cations. If one may disregard for the moment the slight variation in the amounts of chloride added with barium chloride as compared with the relatively large amount of this ion added with the alkali chloride, it follows that, for a given concentration of different alkali chlorides, the varying amounts to barium that must be added will depend on the effect of each cation on the adsorption of the other. Thus, the adsorption of barium is cut down by lithium ion less that by potassium ion, tending to make the precipitation concentration of barium chloride less in the presence of lithium chloride than of potassium chloride. Hand in hand with this is the decrease in the adsorption of alkali by barium, which will tend to make the precipitation concentration of barium chloride higher in the presence of lithium. From this point of view, the latter factor appears to predominate with the alkali chlorides. With hydrochloric acid, however, the cutting down of the adsorption of barium by hydrogen ion is the determining factor with lower concentrations of hydrochloric acid; while with higher concentrations of acid the second factor appears to predominate," p. 99.

"Knowing the conditions favorable to jelly formation by precipitation of a negative colloidal hydrous chromic oxide, it is a simple matter to precipitate the positive sol as a jelly. All that is necessary is to add just enough electrolyte to cause complete coagulation in an hour or two. If too little electrolyte is used, precipitation is incomplete and the results are unsatisfactory; while if too great an excess is added, the precipitation is so rapid that a gelatinous precipitate is formed. From the results recorded in Table X, it is quite evident that jellies will form in the presence of any precipitating ion. Moreover, the hydrogen concentration within which jellies will form, can vary over a wide range; thus, they are obtained from strongly alkaline solution and from a colloid stabilized by hydrogen ion," p. 102.

"Recently Willstätter and Kraut described a number of hydrous oxides differing in reactivity and adsorptive power, by precipitating aluminum sulfate with ammonia: With concentrated ammonia, and boiling for a long time, the precipitate was a pale yellow plastic mass *A*; without prolonged boiling, it was a very pale yellow plastic mass *B*; with dilute ammonia it was a pure white, very voluminous, and very finely divided substance *C*. An intermediate variety *b* prepared by the dialysis of aluminum chloride with frequent additions of small quantities of ammonia, was claimed to be related chemically to *B* but resembled *A* in adsorptive capacity; and a modified form of *C* precipitated at 60° had an adsorptive capacity similar to *B*. Specimens of *A* were entirely different in properties, depending on whether they were still moist or subjected to a rapid preliminary drying in a high vacuum over P_2O_5," p. 103.

"The adsorption of chromate by hydrous alumina is sufficiently strong to impart a yellow color to the precipitate formed in the presence of alkali chromate or precipitated and subsequently shaken with alkali chromate solutions. Charriou found little alkali metal in the precipitate and so attributed the color to the formation of aluminum chromate on the surface of the alumina. There is no justification for this conclusion and it is probably erroneous. If well-washed alumina is shaken with alkali chromate, the solution becomes alkaline owing to stronger adsorption of acid than of base. The yellow color is due to chromic acid rather than aluminum chromate. Ishazaka found that potassium dichromate was converted to chromate in the presence of powdered alumina," p. 126.

"It cannot be emphasized too strongly that comparative data on adsorption by hydrous alumina or any other substance cannot be obtained unless particular attention is paid to the physical character of the adsorbent. To make the most rapid progress it would seem to be essential for biochemists to get together on some well-defined arbitrary methods of procedure for making a series of preparations that could serve as standards. The systems with which the biochemists deal are so complicated at best that there seems no justification for carrying out adsorption experiments with adsorbents that are not standardized in some way," p. 129.

"Since a crystalline rose-colored oxide [of cobalt] is known with certainty, and there is only an analysis of an apparently amorphous mass to indicate the nature of the blue preparation, it might be concluded that the blue compound is a hydrous oxide and the rose, a hydroxide. This hypothesis, like that of Hantzsch's, cannot be correct, since it is based on the manner in which water is held by the oxide, and apparently we may have either a blue or a rose oxide in the absence of water. Thus cobalt glass owes its color to the blue anhydrous oxide; and the brown anhydrous powder obtained by drying the precipitated hydrate melts without decomposition and gives rose-colored crystals on cooling. This suggests the possibility of the color of cobalt oxide and hydroxide being determined by the size of particles. In glass the particles are obviously highly dispersed and appear blue, while the oxide in mass is red. Similarly, the precipitated oxide is most finely divided when first formed and so is blue; but in the presence of a slight excess of alkali, the highly hydrous mass ages, losing water and becoming denser, the color at the same time changing from blue through lavender to rose. The rate of this transformation is, of course, hastened by raising the temperature, and is retarded or stopped by the presence of basic cobalt salts or hydrous nickel oxide.

"If one objects to attributing the difference in color to the size of particles, an alternative hypothesis is that there are two allotropic forms of cobalt oxide, an instable blue one and a stable rose. As a matter of fact, the transformation of the blue gelatinous oxide to rose in the presence of alkali has led people to regard the former as the alkali-instable modification and the latter as the alkali-stable modification. The existence or non-existence of allotropic forms could probably be settled by comparing x-radiograms of the blue and rose oxides or hydrates," p. 149.

"In general, Patrick finds the adsorption of a solute to increase as its solubility in the solvent decreases. For example, the adsorption of benzoic acid from the several solvents is in inverse order of its solubility in these solvents. Similarly, formic acid is much more strongly adsorbed from toluene than is the more soluble butyric acid; iodine is adsorbed to a small extent in accord with the same laws. Moreover, nitrobenzene is adsorbed to a very great extent from kerosene with which it is only partially miscible, while benzene, which is much closer to kerosene in the solubility series, is adsorbed to a considerably smaller extent," p. 185.

"It should be pointed out that the capillary theory of adsorption is strictly applicable only in case there is not a specific adsorption factor in addition to the purely capillary phenomenon. Thus in the case of activated carbon the chemical polarity of the adsorbent cannot be disregarded and the results cannot be interpreted solely in terms of the physical nature of the capillaries. Moreover, the adsorption of solids from solutions does not come within the scope of the capillary theory," p. 188.

"Kramer finds that the addition of animal or vegetable oils to a 0.2 percent solution of sodium silicate gives a fine stable emulsion in which many of the drops exhibit Brownian movement. The fatty acid of the oil combines with the alkali to form soap, liberating colloidal silica which acts as a protective colloid for the emulsion. The careful addition of dilute hydrochloric acid produces a silica gel emulsion, while the addition of lime water causes coagulation froming a cheese-like coagulum and a thin liquid. These experiments are said to reproduce synthetically the changes in the tissue which take place in tuberculosis. Alkali silicate forms a fat emulsion in the tissues. The hydrous silica in the emulsion has a strong affinity for lime which is withdrawn from the blood and causes the caseation of the emulsified fat as in the experiments referred to above. Carbonic acid then acts slowly on the 'silica cheese,' converting the lime into carbonate, a process designated by the pathologists as calcification. There remains in the tissues the small amount of hydrous silica which served originally as the protective colloid for the emulsion. In line with this, Neyland found in tubercular lymph glands of oxen, a silica content of 0.27 gram SiO_2 in 1 kilogram of dry tissue while a calcified lymph gland contained 1.54 gram SiO_2 per kilogram of tissue," p. 195.

"There seems to be no real justification for postulating the existence of a wide variety of condensed stannic acids and complex basic salts. It seems much more likely, particularly in the light of the recent observations of Pascal and Yamada, that the various products are simply hydrous stannic oxides that have adsorbed hydrogen and chloride ions, the positive charge on the colloidal particle arising from preferential adsorption of hydrogen ion," p. 208.

"Probably the most interesting property of vanadium pentoxide sol is its double refraction on stirring, a phenomenon first observed by Freundlich and his pupils. If stirred with a glass rod and viewed in reflected light, an aged sol appears to be filled with yellow glittering streaks as if there were fine crystals suspended in it. In transmitted light, the sol remains clear, but dark streaks can be observed. Viewed between crossed nicols, the field remains dark as long as the sol is not disturbed; but stirring causes the field to become bright at once. By allowing the sol to flow between crossed nicols in convergent light parallel to the line connecting the nicols, an image is obtained of a crossed axis with concentric rings. Observed with a quarter-wave mica plate, the flowing sol behaves like a positive uniaxial crystal. Freundlich pictures the sol at rest as made up of elongated particles possessing the usual unordered Brownian movement which can give no double refraction. The setting up of directed motion causes the sol to lose its isotropic nature and to become double refracting. A section cut from the sol may be looked upon as having a space lattice somewhat similar to

a plate from an optically monoaxial crystal, the long axis of the sol particles coinciding in direction with the optical axis," p. 266.

"The double refraction in an aged sol is so strong that it can be demonstrated by allowing the sol to flow through a prismatic trough with a triangular cross-section and using this as a prism to decompose spectrum lines. In this way, the red hydrogen line is resolved into two oppositely polarized lines. The more strongly refracted ray vibrates parallel to the direction of flow of the sol, and in accordance with Babinet's rule, this extraordinary ray is more strongly absorbed that the other," p. 267.

"A mixture of perborate and permanganate may be added to bath water to make what is known as an 'oxygen bath'. The reaction in solution gives hydrogen peroxide and colloidal manganese dioxide, and the latter catalyzes the decomposition of the former, setting free oxygen which forms a supersaturated solution in the water and is subsequently evolved in small bubbles on the skin of the bather. The presence of electrolytes in the bath water was found to have such a marked effect on the rate of evolution of oxygen that Lottermoser investigated quantitatively the influence of various alkalies and salts on the decomposition of hydrogen peroxide by manganese dioxide. The impurity was added to the peroxide solution, after which the catalyst was prepared directly in the solution by adding permanganate and base in the order named. With salts of a common anion, different cations influenced the decomposition in the order $Ba^{\cdot\cdot} > Sr^{\cdot\cdot} > Ca^{\cdot\cdot} > Na^{\cdot} > K^{\cdot} > Li^{\cdot}$, barium ion accelerating it the most and lithium ion retarding it the most. Unfortunately, Lottermoser did not inquire into the reason for the accelerating action of certain electrolytes and the inhibiting action of others; but it is probable that this is very closely related to the adsorbability of the cations and to the variation in physical character of the hydrous particles formed in the presence of different electrolytes. $Mg^{\cdot\cdot}$ and $NH_4^{\cdot}$ ions were found to have a marked retarding action by cutting down the concentration of hydroxyl ion. For preparing a satisfactory oxygen bath, it is obviously necessary to avoid waters containing magnesium salts," p. 296.

"After championing the use of thermodynamic formulas to interpret tanning by tannin, one wonders why no attention whatsoever seems to have been paid to the phase rule in interpreting the results with chrome tanning. In the light of this generalization, the curves obtained by Thomas and Kelly certainly do not offer convincing proof of the formation of chromium collagenates. On the contrary, they indicate that quite the opposite is true," p. 330.

"The purification of water on a large scale is carried out with one or more of the following objects in view: first, to render the supply safe and suitable for drinking; second, to reduce the amounts of mineral ingredients which are injurious to boilers; and third, to remove substances injurious to the machinery or the manufactured product in industrial processes. The colloidal matter in surface waters consists of finely divided particles of clay, sand, organic coloring matter, and bacteria. Such material can usually be removed by agglomeration and filtering under suitable conditions. Undesirable dissolved substances such as the bicarbonates and sulfates of calcium and magnesium can be eliminated only by resorting to chemical precipitation. Many of the largest artificial water purification plants are operated solely to provide potable water without special attention to its use for industrial purposes. In other instances, the water is not only rendered potable but is softened at the same time. A notable example of the latter is the purification plant at New Orleans where hard, colored, turbid, sewage-polluted water from the Mississippi River is rendered suitable for industrial as well as domestic consumption.

"The most important requirement in the purification of a municipal water supply is the elimination of bacteria, especially those causing disease, and the removal of turbidity; but a perfectly acceptable drinking water is free from objectionable odor, taste, and color. Small amounts of the mineral constituents commonly found in water are not objectionable, as a rule, but certain ones are highly undesirable. Thus, the presence of as little as 2 p.p.m. of iron renders the water unpalatable to some people and causes trouble by discoloring washbowls and tubs, and by producing rust stains on cloth. It is needless to say that drinking

water must contain no more than a trace of salts of barium, copper, zinc, and lead, because of their poisonous character. Fortunately, the occurrence of harmful amounts of the latter salts in the ordinary water supply is quite rare," p. 366.

"In view of the importance of aluminum ion in the coagulation and removal of coloring matter, it would appear advantageous to treat highly colored waters at a low pH value where aluminum ions exist in solution as such, followed by increasing the pH value in order to precipitate all the aluminum. This is exactly what Norcom does with Cape Fear River water at Wilmington, N. C. The desired result is accomplished by connecting two sedimentation basins in series, treating the water with alum at a low pH value in the first basin, and increasing the pH value in the second basin by the addition of alkali," p. 378.

"Nitrogen in the form of nitrate is preferred by most plants; but, as already noted, the element cannot be stored as nitrate since the latter is so weakly adsorbed by the soil colloids that it is readily leached out and lost. The original source of nitrogen for plants, other than the legumes, is organic matter which is changed by the action of bacteria into ammonia and subsequently into the relatively strongly adsorbed ammonium salts. The latter transformation is a result of the soil acidity which is derived in large measure from the hydrolysis of salts and the relatively stronger adsorption of base than of acid by the soil colloids. Under the influence of bacteria, the small equilibrium concentration of ammonium salt is oxidized slowly to nitrate and becomes available for plant food," p. 404.

This is an admirable book. This reviewer has already found help in it for his research work and he expects to profit much more from it as time goes on. It is to be hoped that the author will continue his good work and will write about other salts, the sulphides for instance.

Wilder D. Bancroft

Magnetism and Atomic Structure. *By Edmund C. Stoner. 22 × 15 cm; pp. xiii × 371. New York: E. P. Dutton and Company, 1926.* "In this book an account is given of magnetic phenomena, and of the attempts made to interpret them in terms of the quantum theory which has been so successfully applied to the general problem of atomic structure. The basis of the quantum theory is still obscure, and its formulation uncertain, and there are many gaps and difficulties in its development. Some of these become especially prominent in magnetism, which was for long regarded rather as a stumbling-block for the quantum dynamical atomic theory. Closer consideration, however, shows that it actually yields remarkably strong support for it. It seems certain that the further study of magnetic phenomena, instead of undermining the quantum theory, will greatly strengthen it as a coherent whole, and will possibly throw light on its essential significance. For this reason, magnetism has at present an immediate importance much wider than that arising from its own intrinsic interest," p. vii.

The chapters are entitled: historical introduction; classical electromagnetic theory; experimental methods and survey of earlier results; the interpretation of magnetism as an atomic phenomenon; the quantum theory; survey of later experimental results—para- and ferro-magnetics; discussion of results—elementary moments and intrinsic fields; the gyromagnetic effect; the magnetic deviation of atomic rays; the Zeeman effect; other magneto-optical effects; diamagnetism; miscellaneous magnetic effects; magnetism and the structure of the atom; magnetism and chemistry; problems—summary and conclusion.

"There was of course a difficulty in the simple electron theory of magnetism in that electrons rotating in orbits should radiate, according to classical theory. For this and other reasons there have been many abortive speculations centering round the view that the electron, even when not rotating in an orbit, is also a magneton—consisting, that is, of a swirl of electricity with the properties of a magnet. These views, frequently ingenious, and of mathematical interest, will not be followed up here, for they have been singularly unfruitful; and the difficulties which gave rise to them are part of a much larger problem which is being resolved in a different manner," p. 12.

"The immense amount of work that has been done in the last twenty or thirty years on magnetism has made it possible to trace back the phenomena observed to the atom itself. The magnetic properties of individual atoms may, to a certain extent, be deduced; and the

attempt may be made to link these up with other characteristics. Working in the opposite direction, synthesizing, a clearer idea of mass magnetic phenomena may then be obtained. Moreover, a study of the magnetic properties may throw light on many obscure features in the theory of the atom; looked at from another point of view, the quantum theory may assume new significance; and the solving of many of the problems of radiation will be helped by the key provided by a study of how radiation phenomena are affected by magnetic influences," p. 14.

"From the point of view of magnetic theory the properties of electrons moving in orbits possess particular importance, for it is clear, bearing in mind the relation between moving charges and electric currents, that such orbital electrons will behave to a certain extent as small magnets, constituting, in fact, physical magnetic 'elements.' The difficulties in connection with radiation, however, led to the invention of hypothetical magnetons, consisting of swirls of continuous electricity in the form of rings of spheres which might be supposed to give rise to magnetic fields but not to radiation. There is no experimental evidence for the existence of such magnetons; and as the radiation dilemma applies to electrons in general, the properties of these hypothetical magnetons are of little physical interest; magnetic phenomena must be explained on the basis of the experimental electrons," p. 34.

"A consideration of a grouping of magnetic molecules in isolated pairs brings out clearly the relevant determinative factors in the processes assumed to occur; but so simple a model would hardly be expected to give a complete representation of the phenomena. In particular, the possible increase in intensity after the groups are broken up until saturation occurs seems too small, while the amount of residual magnetism indicated is much less than that frequently observed. It seems necessary to suppose that the molecules can take up more than one equilibrium position; there must be more than one "line of centres" along which a molecule can set itself. Ewing in fact found that groups of four magnets gave a much closer approximation to the facts; and finally he considered continuous distribution in cubical order. In each group the molecules will normally set themselves along lines of centres, sub-groups being formed with lines of centres (and magnet axes) at right angles to each other. It may be noted that if the groups consist of pairs, or possess purely linear symmetry, each group would normally possess its saturation intensity of magnetization; whereas a group with cubical-order distribution of centres could be nonmagnetized. The point is of interest if the groups are regarded as building up constituent crystals of the ferromagnetic material.

"On the molecular magnetic theory retentivity depends on the symmetry of the molecular groupings; while coercivity depends on the strength of the molecular ties. There will thus not necessarily be any general relation between them, as is in fact observed. The theoretical retentivity for the simple groupings considered may be easily calculated. An ordinary piece of ferromagnetic material may be supposed to consist of a large number of groups, with lines of centres distributed at random. After a field is applied to produce saturation and then gradually reduced to zero, the molecular magnets in each group will be left directed along the line of centres making the smallest angle with the field, and in a sense giving a resultant moment in the field direction. Each group will retain its saturation intensity, the directions of the group moments, however, making various angles with the field; these directions will be distributed at random within a cone whose semi-angle a is determined by symmetry characteristic of the groups," p. 61.

"It may be said that in essentials, and independently of the quantum theory, little has been added to the Langevin-Weiss views. The Weiss hypothesis of an intrinsic molecular field proportional to intensity certainly enables an enormous range of facts to be co-ordinated, but the nature of the field remains unknown. Before discussing this, it may be useful to consider briefly the relation between the views of Weiss and Ewing. The control on the elementary magnets in a ferro-magnetic may be regarded, according to Weiss, as arising from an effectively homogeneous field. On Ewing's view, the control arises from the heterogeneity which results from there being strong forces in the immediate neighbourhood of the poles of the elementary magnets which are regarded as possessing finite length. Considering a linear distribution of magnets, on Ewing's view, quasi-saturation would be

approached once the magnets were deflected beyond their neutral equilibrium position; while according to Weiss, in relatively small fields, the magnet axes in an elementary crystal of the type assumed, will point either in one or the opposite direction. Ewing does attempt to account for the mechanism involved; and although the theory is inadequate, and the mechanisms so far proposed do not work, it seems premature to suppose that the whole idea is unwarranted," p. 85.

"From a magnetic point of view the transition elements possess particular interest owing to their paramagnetic characteristics. Paramagnetism occurs for other than transition elements, but not in the simple (polar) compounds where the elements enter as ions. Paramagnetism of atoms or ions is an indication of a lack of symmetry (and so of magnetic balance) of the electron orbits. In the formation of a simple compound there is a gain and loss of electrons by the constituent atoms, the outer electrons of the ion tending to assume an inert gas configuration. In NaCl, to take a simple example, the Na loses an electron, the Cl gains one; the electronic constitution of the ions will be similar to those of the inert gases Ne and Ar, which possess 'completed' configurations. These completed configurations correspond to symmetrical balanced orbital systems with no resultant magnetic moment. The ions of transition elements, on the other hand, will possess all the asymmetry of the incomplete underlying group of electrons which is being built up in them. In $FeCl_3$ the Fe ion contains 23 electrons; of these 18 will be distributed among the K (2), L (8), MI (2), MII (2) and MIII(4) levels, as in Ar; the remaining 5 cannot form a completed symmetrical group, and the lack of balance among the electronic orbits gives the ion a resultant magnetic moment, and ionic paramagnetism occurs. The idea of associating the peculiar properties of the transition elements with the development of an underlying group of electrons was put forward by Ladenburg; it appears in its full beauty in Bohr's theory of atomic structure," p. 178.

"In the correlation of ionic and spectroscopic moments the goal has not yet been reached, but *it is being rapidly approached. Much progress has been made. Amongst the wealth of* detail, there is a liability to lose sight of the astounding fact that from experiments so diverse as those on susceptibilities of salts and solutions, on the magnetic deviation of atomic rays, and on the multiplet structure of spectral lines, accordant conclusions may be drawn as to the magnetic moments of atoms and parts of atoms. Details are generally being fitted into a simple and coherent design, and in the process the quantum theory, which provided the key, is itself being refined and extended," p. 232.

"From his work as a whole Oxley concluded that magnetic phenomena could not be accounted for by atoms of the Bohr type, with large electronic orbits; he inclined rather to a picture of the atom (or molecule) in which the electrons rotated in small orbits about the mean positions assigned to them in the Lewis-Langmuir static models. This seemed necessary to account for the large values of the local fields, assumed to be magnetic, between the molecules; these fields, as has been seen, being in general much larger than those which would arise from Bohr orbits. There is, however, such an enormous mass of evidence in favour of the general Bohr theory, and it accounts with such remarkable success for so many magnetic phenomena, that it is out of the question to abandon it. Moreover, the difficulty as to the magnitude of the molecular fields assumes quite a different significance as soon as the supposition is abandoned—as it must be—that the fields are purely magnetic. There are certainly many difficulties, but, in the light of the discussion which has been given of intrinsic fields in para-magnetics, it seems undoubted that for these and for diamagnetics also, a solution will eventually be found in terms of the general quantum theory," p. 280.

While the chemist will get much profit out of this book, there is a lot that he will have to skip because there is a great deal of the mathematics that is over the head of most of us.

Wilder D. Bancroft

Lehrbuch der physikalischen Chemie in elementarer Darstellung. *By John Eggert. 25 × 17 cm; pp. ix + 539. Leipzig: S. Hirzel, 1926.* The book is divided into three parts. The first is entitled the basis for the atomistic view-point, the chapters being the classical atomic theory and the equations of state with subheads of the elements of thermodynamics,

the elements of the kinetic theory of matter, and the elements of the quantum theory. From this one can see that the author's idea of elementary physical chemistry is primarily thermodynamics and physics, and not chemistry.

The second part deals with what some people call the physical properties of substances. The headings of the chapters are: atoms; molecules; states of aggregation (one-component, two-component, and multi-component systems).

The third part deals with chemical processes and the chapters are entitled: chemical equilibrium and the mass law; thermochemistry; electrochemistry; chemical kinetics; photochemistry.

The author is not very critical. He gives Perrin's work on the distribution of gamboge particles as though it were really accurate, p. 46; he gives the Arrhenius deduction of the osmotic pressure, p. 226, instead of the van't Hoff one; he does not worry over heats of dilution; he does not distinguish between particle size and molecular weight, p. 235; and he is very shaky on his colloid chemistry, p. 233. He says that a number of substances, such as albumin, clay, sulphides, etc., are peptized spontaneously by water (especially on washing freshly formed precipitates). As a matter of fact, these substances are peptized by adsorbed ions, hydrogen sulphide, etc. When precipitates are washed immediately after formation, what happens is that one washes out the excess electrolyte which is acting as a coagulating agent.

The difficulty raised in the paragraph on p. 74 seems uncalled for. "The positive electron is identical with the positive ion of the hydrogen atom. It possesses, like the negative electron, the charge e; but has eighteen hundred times the mass. Its atomic weight is that of the hydrogen atom (1.008). On account of its relation to matter the positive electron is called the proton. This relation is to be accepted with some limitations. Experiment shows that just as the hydrogen atom can take up one electron at most [he means lose one], so the helium atom cannot receive more than a double charge. The doubly positively charged radical, He; contains therefore no more negative electrons [he means valence electrons] and the mass of the proton referred to one charge must have the same m value as the hydrogen ion. Actually the value calculated from He$^{\cdot\cdot}$ is two or practically double the value of 1.008 for He$^{\cdot\cdot}$ This contradiction remains when we pass to the heavier, completely discharged atomic ions (with Li$^{\cdot\cdot\cdot}$ for instance) and is inexplicable at present."

The reviewer is a bit sceptical about a statement on p. 162. Hydrochloric acid crystallizes at 190° absolute to a face-centered cubical lattice (probably as molecule), while below 98° absolute, another, more complicated, lattice appears. The reason for this is the motion of the particles in the lattice due to heat. At the higher temperatures, this motion is quite violent, so that the details in the field structure of the hydrochloric acid molecule become blurred and the cubical symmetry appears. At lower temperatures the movement due to heat is less, the differentiated condition of the field begins to show, and the change into the new state of equilibrium follows."

There is a very definite paragraph on steam distillation, p. 211. "If one heats water with nitrobenzene, the system boils at 99° under atmospheric pressure. The partial pressure of the water is about 74 cm and that of the nitrobenzene about 2 cm. Although the partial pressure of the nitrobenzene is only 2.64% of the total pressure, the distillate contains so large a weight percentage of nitrobenzene as to make the process advantageous, because the partial pressures are a function of the molar concentration in the vapor phase. For every mol of water distilled, 2.7% mols of nitrobenzene come over, or 3.3 g nitrobenzene per 18 g water, or 16% by weight. Distillation with steam can be used with high-boiling substances in spite of the low partial pressure, provided the molecular weight of the substance to be purified is several times as large as that of water."

There is a valuable table on p. 291, giving the chemical constants for Nernst's heat theorem for twenty-odd substances. In other pages there are tables which the reviewer was glad to see; but, considered as a whole, the book is distinctly a mediocre one.

Wilder D. Bancroft

Theoretical Metallurgy. *By Reginald Scott Dean. 23 × 15 cm, pp. 246. New York: John Wiley and Sons, 1924. Price: $3.00.* In the preface the author says: "The present volume is the result of a demand for a second edition of the author's translation of Schenck's "Physical Chemistry of the Metals." When an attempt was made to revise that text, it soon became apparent that if an adequate revision were made very little of the original text would be left. The title has therefore been changed to indicate the somewhat broader field covered. . . . The book does not claim to be comprehensive; it does aim to be suggestive. . . . Some two thousand references have been given, to allow the reader to pursue the subject further."

The book is divided into two main parts, the first considering the properties of metals, the second taking up the theory underlying the various metallurgical processes. The properties are considered from the modern point of view of crystal structure as developed from X-ray analysis and are discussed under the headings: metals, metallic compounds, and metallic alloys. The metallurgical processes in turn are classified as (1) processes not involving chemical reaction and (2) processes involving chemical reaction. Under the first group of processes appear topics as thermoelectricity and thermocouples; permanent magnets; extrusion of metals; bearing metals; alloys of great hardness; welding and soldering; hardening of steel; ore flotation; and corrosion, though in many cases the treatment is necessarily very brief. Under the second class of metallurgical processes are considered the application of the Phase Rule, the Mass Law and the Theorem of LeChatelier to metal systems, together with the question of reaction velocity; the oxidation and reduction of metals; the blast furnace processes; the reaction of sulphides, phosphides, silicides and arsenides; and theory of metallic catalysts.

On page 4 the author defines the metallic state by enumerating properties which are characteristic of the metals, as follows:—

"1. Metallic luster, or the nearly complete reflection of light from the surface.
"2. High electrical and thermal conductivity.
"3. Thermoelectric, thermionic, photoelectric and similar effects.
"4. Malleability.
"5. Monatomic condition in the vapor state and in solution in other metals.
"6. Tenacity of gas adsorption."

On pages 47-49 metallic luster is considered. "The characteristic luster known as metallic is produced by a complete reflection of light. From the electromagnetic theory of light it follows that any substance which is a good conductor will give practically a total reflection of light. . . . Metallic luster is shown by substances which are not metallic, if for any reason they give nearly complete reflection. Thus, air bubbles under water appear metallic, as do some aniline dyes. In the latter case, however, only certain colors are completely reflected; these are the colors which correspond in frequency to the semi-bound electrons responsible for the color of the dyes. . . . Thus a piece of fuchsin paper appears like a piece of green metal."

On page 49 the author accounts for thermo-electric force as follows: "The thermo-electric force caused by the contact of two metals may be considered as the result of electron diffusion. At such a contact the electrons tend to flow from the metal with the higher electron pressure to the one with the lower. This tendency to diffuse is balanced by the electrostatic forces set up by the loss and gain of electrons.

"If a couple is then made of two junctions of different metals and these junctions held at different temperatures, the diffusion tendency will be increased at the hot end and there will be deficiency of electrons at the hot end of the metal with higher electron pressure, and the electrons will therefore flow from the cold to the hot end. In the metal with less electron pressure, the electrons will flow from the hot to the cold end.

"The electromotive force developed in the circuit will depend on the rate of diffusion. The rate of diffusion is determined by the difference of electron pressure and the difference of temperature, in a way entirely similar to the electromotive force of electrochemical diffusion cells."

During the discussion of the thermionic effect, the following interesting statement appears, p. 51: "The emission of electrons is strictly comparable to an evaporation process, and is accompanied by an absorption of heat. From a consideration of these evaporation relations it is possible to get the specific heat of electricity. This quantity, however, varies both with the temperature and the metal, being positive for mercury, copper and silver, and negative for platinum and iron."

In connection with the consideration of hardness the author observes that "with solid solution *there is always an increase in hardness and correlated properties. Thompson* has pointed out that the greatest increase in hardness is obtained when the two metals are of widely different atomic volume. From this he reasoned that the hardness was due to a distortion of the lattice at the points where the solute entered, this distortion interfering with the mechanical deformation. This is essentially in accord with the view of Jeffries and Archer who, however, considered that the atomic forces are increased by the greater *attraction of unlike atoms. Rosenhain has placed the distortion theory on a quantitative* basis. He assumes that the hardness produced by a given percentage of a second metal in solid solution is proportional to the distortion of the lattice and that the saturated solid solution represents the maximum distortion which the lattice will stand. Accordingly, the hardness produced by a given percentage of the second metal is inversely proportional to the solubility of that metal."

To one interested in colloids, the following discussion, pp. 112-114, is significant. "The formation of disperse systems in alloys is a matter of great importance. Gillett has recorded the effect of colloidal suspensions in molten brass, and the formation of plastic bronzes from copper and lead is a strictly colloid chemical process. The two metals are rendered miscible at high temperatures by means of a third substance, as sulfur or antimony and then cooled quickly so as to give the separating lead a disperse form.

"In the realm of solid alloys, disperse forms are quite common. According to Benedicks, troostite represents a colloidal distribution of iron carbide in iron and this view has been extended to cover practically all the transition products between austenite and pearlite.

"This dispersion of a newly formed solid phase in ultramicroscopic form is also exhibited by alloys of nickel and iron and of cadmium and tin, as well as for the solid solution of copper in zinc.

"A case which has been studied recently in great detail is that of duralumin, an alloy of copper and aluminum which presumably contains $CuAl_2$ in a state of dispersion." . . . If the facts concerning the change of crystal properties with size of grain be extrapolated to the region of colloidal dimensions, it follows that colloidal dispersions will be very much harder than aggregates of large particles of the same components. The properties of colloidal dispersons do not, however, form a transition stage between aggregates and solid solutions, since, in general, the solid solutions are softer than the highly disperse mixtures of the same components. For example, the solid solution of $CuAl_2$ in aluminum which is present in unaged duralumin is not so hard as the disperse system caused by the separation of the $CuAl_2$ as fine particles on aging. There is thus a region, the so-called critical dispersion, or zone of maximum colloidality, which possesses the maximum hardness."

Another interesting case involving the formation of an emulsion appears on page 136. "The other type of bearing metal is known as plastic bronze; its components are usually copper and lead. These two metals are immiscible in the liquid state, and the successful manufacture of a plastic bronze depends on the solidification of a fairly homogeneous emulsion of the lead in the copper. The methods of preparation belong to a discussion of colloid chemistry. They consist essentially, however, in adding some substance, as sulfur, which increases the solubility of lead in copper at high temperatures, and then cooling suddenly so that the emulsion which forms by the separation of the lead is preserved in the solid state. A microphotograph of a typical plastic bronze is shown in Fig. 56."

The unsatisfactory state of our knowledge about soldering fluxes is evident in the following quotation, p. 150:—In soldering, the essential thing is to get a wetting of the surface with the solder. . . . "There are two forces acting on a ball of solder on a metal surface, the surface tension, p, acting tangentially to produce a spherical surface, and the

wetting effect, W, acting along the metal surface. This latter is a complex quantity and depends upon several things, particularly on the flux used. The fluxes which cause the greatest amount of spreading are zinc chloride, stannous chloride, and ammonium chloride. It is a matter of considerable importance in manufacturing to know the principle on which these fluxes act. Very little data exist in the literature on this point.

"The action is not entirely one of dissolving oxide, as a cleaned copper surface may be coated with rosin to prevent oxidation and still the spreading will not be comparable to that obtained with zinc chloride on a comparatively oxidized surface.

"The effect of surface tension cannot be an important one, since there are other salts with as high or higher surface tensions which are entirely ineffective as soldering fluxes. It may be suggested as a possibility that at the temperature of soldering the soldering fluxes give up hydrochloric acid which replaces the adsorbed air on the metal surface and is subsequently removed by the solder."

The author has succeeded in writing a very interesting book, even though the discussion is rather fragmentary in some places, and anything but clearly expressed in others, especially in the second part of the book where the phase equilibria are considered. Also the reviewer does not like the statement, p. 36, that in transition cells dealing with two metallic modifications, the modification which is out of equilibrium is the positive pole. However, the work is suggestive and in that sense amply fulfills the author's promise as stated in the preface.

T. R. Briggs

Physical and Chemical Constants and Some Mathematical Functions. *By G. W. C. Kaye and T. H. Laby. Fifth edition. 24 × 16 cm; pp. 161. London: Longmans, Green and Co., 1926.* The fact that 'Kaye and Laby's Tables' have passed through five editions in fifteen years, during which period they have been widely used by workers in very varied fields, gives a security against accidental errors which no new publication can afford. The task of keeping such a mass of data up to date has been effectively carried out in most sections, but those relating to surface tensions, specific heats of gases and heats of formation may be mentioned as being in some need of further revision. With regard to the subject matter, it is, of course, impossible to satisfy everyone's needs in a limited space, but it might have been expected that the present edition would contain some additional matter besides a table of isotopes. On the more chemical side, values of such quantities as chemical equilibrium constants, free energies, electrode potentials and solubility products would have been welcome. Information on these subjects is so frequently required that its provision would have greatly increased the range of usefulness of the book without necessitating any appreciable increase in its size.

No changes having been made in the arrangement of the material, the setting of the type or the binding of the book, it only remains to commend the volume as the most useful and reliable collection of physical and chemical data contained within such a conveniently small space.

H. J. T. Ellingham

STRUCTURAL COLORS IN INSECTS. II

BY CLYDE W. MASON[1]

Iridescent Colors

Iridescence has for its main characteristic a change in the hue of the object exhibiting it as the angle of vision is varied; frequently iridescence is associated with marked surface lustre, which is more or less pearly or metallic. Whatever may be one's aesthetic standards, there is something peculiarly fascinating about the glinting, shifting hues shown by iridescent objects, and those which occur in nature have attracted their share of attention because this property is so markedly different from the ordinary sort of coloring. There are numerous familiar examples: certain insects, mother-of-pearl, oil films on water, tarnish on metals, diamonds and prisms, peacocks and hummingbirds, "lustre" pottery and glasses, opals, laboradorite, "Barton's buttons" and so on. One might even call "changeable" or "two-tone" silks iridescent, though in this case it is only a question of one lot of colored threads being in the proper position to reflect light while those of the other color are in an unfavorable orientation. Microscopically this is hardly iridescence, but macroscopically it satisfies the criterion.

It is commonly assumed that iridescent colors are probably of structural origin but a more definite explanation than this is necessary, and many extensive studies have been made of the different types of iridescence, and their occurence in nature. Most works on physical optics devote a fair amount of space to the discussion of the principles underlying these phenomena, and to the criteria which may serve to identify them.

The iridescence observed in insects has been ascribed to almost every possible cause, but in most cases the problem has been attacked from one angle only. For instance, by certain quantitative optical tests a marked resemblance has been shown between the colors of certain beetles and those of certain solid dyestuffs, which give metallic reflection; however, the same tests have not been applied to film colors, to which they also bear striking resemblances. There has also been a good deal of reasoning of this sort: a grating has many lines, close together and regularly arranged, and it gives iridescent colors; certain scales of insects have many lines, close together and regularly arranged, and they show iridescent colors; therefore, the colors of the insects must be due to the grating structure. More than this is necessary, of course; it must be shown that in all observable respects the colors are identical with those obtained from gratings, and also that *they cannot be due to any other possible cause*. In the case just cited, the lines are present. They must act as a grating and they do; but the grating colors under ordinary conditions are not observable, and the colors seen are undoubtedly due to a different cause.

[1] The investigation upon which this article is based was supported by a grant to Messrs. Bancroft, Chamot and Merritt from the Heckscher Foundation for the advancement of Research established by August Heckscher at Cornell University.

In the work on structural colors of feathers, carried on at Cornell three years ago[1] it was necessary to study various types of structural colors; and tests were developed which served very positively to identify those present in feathers, namely, Tyndall blue and thin-film colors, and to exclude the other possibilities. All the "metallic" or iridescent feathers studied were found to owe their colors to thin films, but in the insect world such uniformity is hardly to be expected. The work on feathers involved a study of the different possible causes of their iridescence, and the same methods of distinguishing between these are applicable to the different cases of iridescence in insects.

Without repeating the whole discussion of the various types of structural color, for which the reader is referred to these earlier articles, the main types of iridescent insect colors will be considered, classified first with respect to their anatomical occurrence.[2]

Iridescent Wing Membranes

The changing colors of the wings of many dragonflies, beetles and other membranous winged insects recall the iridescence of soap bubbles, and although this is largely assumption on the part of most people, Goreau[3] established their nature by a very sound and logical study.

Obviously, the colors are structural, for they are observable in wings which are wholly unpigmented, as well as in pigmented wings after bleaching. The variety of coloring and its intimate mingling in such small area also make considerable demands upon any theory of their pigmental origin, while the undiminished iridescence in specimens bleached to colorless transparency is radically different from the selective metallic reflection (surface color) of strongly absorbing substances such as dyestuffs. They appear with full brilliancy in highly diffuse light, and are seen from any azimuth, along the line of direct reflection from the wing surface, so they cannot be due to structure of the nature of diffraction, gratings or prisms, all of which require sensibly unilateral illumination, and show their coloring in directions out of the line of the direct beam, and in one plane only (unless an infinite number of crossed gratings or prisms be postulated). No indication of any such structures is observable by microscopic examination.

Other special cases of diffraction phenomena are also eliminated by the above simple observations, for there is no "scattering" of light other than that due to the "pebbled" surface of the wing membrane, nor is there any evidence of haloes or coronas from any fine granular structure.

A more detailed study of the specimens in questions throws additional light upon the nature of these colors. The common house-fly affords an example. Its unpigmented wings exhibit highly variegated colorings, mostly reds and greens, when examined closely with the naked eye or with a low-

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[1] Mason: J. Phys. Chem., **27**, 201, 401 (1923).

[2] The insects studied in this paper were furnished through the kindness of Dr. W. T. M. Forbes, of the Department of Entomology at Cornell. The writer is also indebted to Dr. Forbes for many helpful suggestions during the progress of the investigation.

[3] Ann. Soc. Ent. fr., (2) **1**, 201 (1843).

power magnifier. These are mingled together wholly at random except near the edges of the wings where they appear in zones. The colors are seen very clearly by reflected light, when observed along the line of direct reflection; and any given point on the surface of the wing changes color as the angle of vision is increased. This change may be from red to green, or *vice versa;* the zones of color near the edge of the wing appear to move outward as the line of vision approaches grazing incidence.

"The "pebbled" surface of the wing membrane prevents the observation of any definite polarization effects by reflected light; such a surface has of course no definite "polarizing angle" and one sees little more by using an analysing nicol prism than without it.

The above surface structure also prevents the effective application of pressure, for such severe tangential strains must result when attempt is made to flatten the "embossed" surface and to compress the membrane that disruption of the structure is likely to result. However, there seems to be a slight shift in the hue of the reflection color, but this is not to be observed with certainty.

When examined by transmitted light the membrane shows only very pale tints which are complementary to those of the same areas seen by reflection.

Swelling agents such as NH_4OH, water vapor, or phenol vapor alter the hues markedly, causing reds to change to greens, and *vice-versa;* these color changes are reversed on the removal of the swelling agent. Immersion in liquid of $n = 1.5$ destroys the color, which is restored by washing and drying.

The iridescent wing membranes of many common beetles show much the same optical behavior as those of the housefly, but present some significant differences. They are pigmented a neutral brown; their reflections resemble the "temper colors" of steel, both in hue and in metallic lustre, and range from blue through purple to yellowish brown nearer the edges and tips of the wings. The changes with increasing incidence are marked, and take place in the order just mentioned; on swelling, the change is in the reverse direction. Bleaching does not alter the hue, though the lustre is less in the bleached specimen.

Splitting the lamellae of the wing apart does not destroy the iridescence; the original colors are seen only on the outer surfaces. The inner surfaces may show different iridescent colorings.

Collodion impressions of either surface show no iridescence, and no structure but the fine wrinkles and stubby hairs of the wing membrane.

Immersion of the wing in liquids of index of refraction *ca.* 1.5 does not result in complete destruction of the iridescence, though the brilliancy of the coloring is very markedly decreased; penetration of the wing of liquids which fill the space between its upper and lower lamellae does not destroy the iridescence.[1]

In addition to the above-mentioned examples, a number of other insects were examined with respect to the same properties, *Tylope laricis*, *Mesothemis*

[1] Goreau thought that the interlamellar air space was the color-producing film.

simplicicollis, *Enallagmae*, *Dolichopus canaliculatus*, as well as the wings of several beetles; these all show substantially the same behavior as regards their iridescence, color change with swelling, sequence of colors on the wing, and absence of any but a neutral pigment. The disappearance of color on immersion seems to be peculiar to the wings of the housefly, however.

Nature of Iridescent Coloring of Wing Membranes

Since pigment coloring and diffraction phenomena as causes of the iridescence are eliminated, the most obvious explanation is on the basis of the colors of thin films, and the behavior described above is in good agreement with this very common assumption. Iridescence is the most striking property of thin-film colors, and their definite sequence of hues (Newton's series) is almost as well known: As the thickness of the film in question increases, a succession of colors occurs which is characteristic to one who is familiar with this series. The series is *not* a spectrum, and the color changes are not to be described in terms of wave-length, but rather as of higher or lower "order," the latter corresponding to the thinner films. Increasing the angle of incidence is equivalent to thinning the film[1] and the colors change accordingly. Swelling or compression of the color producing films alter their thickness, and consequently their color. The very pale tints observed by transmitted light are due to the large admixture of white transmitted light. Against a dark background the reflection colors are complimentary to those transmitted, and of considerable saturation and brilliancy.

With respect to all the above properties, the colors of iridescent wing membranes correspond closely with those of thin films; however, certain discrepancies must be considered before their identity can be called established. If a thin color-producing film is brought in contact with a medium of index of refraction near its own, it should show a very marked diminution of its color, with complete disappearance if the index of refraction is matched exactly. In the case of the common housefly this is readily observed, but with the other wings examined only a decrease in the intensity of the color takes place, even when the wing membrane is immersed in liquid of refractive index near that of chitin. This same behavior is found in the case of iridescent feathers, and is best explained on the assumption that the color is produced by multiple thin films, only the outer one of which would have its action affected by contact with a medium of similar index of refraction. We ordinarily think that a thin film must have a markedly different index of refraction from the surrounding medium if it is to produce color and appear metallic. However, a single thin film of xylene ($n = 1.49$) on glass ($n = 1.52$) shows Newton's series of colors distinctly as it evaporates. The brilliantly lustrous and iridescent flakes that fall from the surface of ancient Roman or Egyptian glass consist of thin laminae (of SiO_2?); they offer a convenient "model" for the study of multiple films. When dry, their reflection is highly metallic and their transmission colors are much more saturated than those of a single thin film. If one of these flakes is immersed in liquid, so that the voids between the laminae are filled,

[1] C. V. Boys: "Soap Bubbles," 148, 151 (1912).

its color and lustre are somewhat diminished; but the index of refraction of the immersion medium must be almost identical with that of the films if all reflection color and lustre are to be destroyed. The iridescent crystals of potassium chlorate studied by Stokes[1] and the fiery patches in the opal are other examples of multiple films in optical contact with a solid medium having nearly the same index of refraction as their own.

The effectiveness of such a color-producing system depends on the difference in indices of refraction and on the number of films; both of these factors may be relatively small without serious loss of saturation or lustre.

The saturation and brilliancy of the colors of even the brightest iridescent wing membranes are closely rivalled by those of artificial thin films such as can be made by allowing a drop of gold size to spread over water. Such a film, after it hardens, may be picked up on a piece of wet paper (preferably gray or black, to give a dark background) and the distribution and sequence of its hues, compared with those of the insects, show a most striking similarity. As for the more or less metallic lustre exhibited by the iridescent wing membranes, this is no more marked than that shown by artificial thin films. If multiple films are present in the wing membrane they might be expected to cause somewhat greater saturation and lustre than a single thin film, but this is opposed by the irregularity and "pebbled" character of the membrane and by its lack of perfect transparency.

Biedermann's explanation of the iridescent colorings of wing membranes as being due to an air film between the two lamellae of the wing[2] is not adequate, although he has recognized the nature of the colors by means of the criteria mentioned above. The thickness of the air film in the interior of the wing is many times greater than that corresponding to the colors exhibited; it may be filled with liquids, or it may be closed or opened by pressure or splitting without altering the colors.

The highly intricate mingling of colors in a small area of a continuous membrane would involve an extremely complicated pigment distribution, if such were possible, but is readily accounted for by slight variations in the thickness of the color producing film. This is confirmed by the fact that these variations of color do correspond to relatively gradual variations in thickness rather than being a mosaic of sharply outlined areas of different colors, and moreover the colors adjacent on the membrane are those adjacent in Newton's series. This is particularly striking near the edge or tip of the wing, where a definite sequence of color zones, (first three "orders" of Newton's series) corresponding to a gradual decrease in thickness, is observed. Such a structural condition is just what one would expect, and conversely, where veins extend out to the edge of the wing, the color zones are altered in a manner that indicates increased thickness near the vein.

Swelling with water or other reagents causes the zones of color to shift toward the edge of the wing, without other alteration of their hues or se-

[1] Wood: "Physical Optics," 161 (1911).

[2] Handbuch der vergl. Physiol. 3, I, 2, 1657 (1914).

quence; on drying, the color zones shift back again to their original positions.

Microscopic demonstration of the actual structure is hardly to be hoped for since the thickness of the films as calculated (*ca.* 0.2μ) must be practically at the limit of resolution, and this limit may be reached only with good "contrasty" objects, suitably prepared. In this case undistorted microtome sections of the same order of thickness as the films themselves, together with highly selective staining of the material of the films would be necessary in order to avoid the possibility of spurious diffraction images. Optical tests are certainly more reliable than histological study, in this instance, and they point to a structure composed of a number (say three to ten) of films of materials of different index of refraction (possibly two varieties of chitin) in optical contact and forming a non-permeable tissue which constitutes the two lamellae of the wing. People were right when they guessed that filmy wings must have thin-film colors.

Iridescent Scales

The explanation of the iridescence of butterfly and beetle scales not being so obvious as in the case of wing membranes, almost every writer on insect colors has had a try at it. The presence of striations has suggested a diffraction grating, and this is popularly assumed to be the cause of the color, although most of the later investigators have not fallen into this error. The people who use the terms "diffraction", "refraction", "dispersion", and "interference" indiscriminately and with reference to either gratings or thin films, who speak of "prismatic" colors when they mean iridescent ones, and who believe that "structural color" tells the whole story, are the ones who have perpetuated this untenable opinion. Hagen[1], Biedermann[2], Onslow,[3] Süffert,[4] Mallock,[5] and others, have pointed out that most scales, whether iridescent or not, are distinctly striated, and these writers have offered various other objections to a diffraction theory. Walter[6] emphasizes the fact that the principal striations are lengthwise yet the colors may be seen with the light falling either lengthwise or crosswise of them. He also points out that a grating requires sensibly unidirectional light for the production of colors, while the scales are fully colored in thoroughly diffuse light. Hodgkinson[7] cites the fact that grating colors are always seen out of the path of the directly reflected or transmitted beam, while the scales show specular reflection, and color in the path of the transmitted light.

All these properties of gratings have been known to physicists for many years, while those of the insect scales can readily be tested by anyone, yet the serious discrepancies given above have not been accepted as conclusive evidence against the diffraction grating explanation of iridescence on insect

[1] Proc. Am. Acad. Arts Sci., **17** (1881-2).
[2] Handbuch der. vergl. Physiol. (Winterstein) **3** I, **2**, 1892 (1914).
[3] Phil. Trans., **211** B, 1 (1921).
[4] Z. Morphol Ökol. der Tiere, **1**, 171 (1924).
[5] Proc. Roy. Soc., **85**, A, 598 (1911).
[6] "Die Oberflächenfarben order Schillerfarben" (1895); cf. J. Phys. Chem., **23**, 454 (1919).
[7] "Manchester Memoirs," **2**, (4) (1889).

scales. Dimmock,[1] Kellogg,[2] and Mayer[3] have been content with such an explanation, and Michelson[4] has postulated a "saw-tooth grating" to reconcile the properties of certain iridescent scales (*Entimus imperialis*) with those of diffraction gratings. Such an unsymmetrical structure is hardly consistent with the highly symmetrical properties of the scales in question, and in addition is open to all the objections given above. It will be dealt with further when the insect studied is discussed.

It is possible to illuminate any scale having reasonably regular striations so that it can act as a grating,[5] but this is entirely independent of whether the scale is iridescent or not as ordinarily seen, and is hardly observable without the aid of the microscope. Latham[6] pointed this out many years ago.

The arrangement of scales on butterflies wings is ordinarily not suitable for the demonstration of diffraction colors, on account of the lack of perfect parallelism of the striae and of the scales. In the case of the "Pearl Morpho" there appears to be some chance of observing diffraction colors under natural conditions though only when the direct rays of the sun fall through the wing and are observed from a point somewhat to one side of their path.[7] The colors seen when the wing is studied with illumination corresponding to this are faint, reminding one of those of mother-of-pearl (another case of diffraction colors in nature), and are very non-uniform.[8] They are barely perceptible in the more pigmented Morphos even under the most favorable conditions, and the yellow transmission color seen in the field by some observers is mainly due to pigment and to the complement of the blue reflection.

Dimmock, Onslow and others have isolated the diffraction effect from the other color producing factors present, by making impressions of the striae of the scales in soft collodion and these "replica gratings" may be made "with most Lepidoptera, whether iridescent or not. . . . That all insects, the impressions of whose scales give spectra, do not themselves show iridescence, makes it doubtful whether diffraction is ever a main source of color, especially as it was found that the brilliant scales of *Morpho Cypris*, Westw., and others with the same structure, gave an almost flat impression.[9]"

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[1] Psyche, **4**, 45 (1883).

[2] Kansas Univ. Quarterly, **3**, 45 (1884).

[3] Proc. Boston Soc. Nat. Hist., **27**, 243 (1896-7).

[4] Phil. Mag., (6) **21**, 564 (1911).

[5] A special case of purely microscopic diffraction color is exhibited by many unpigmented, boldly striated scales. The color by transmitted light is a fairly deep blue if observed under the proper conditions, namely: with the aperture of the illuminating beam from the condensor bearing such a relationship to the aperture of the objective that the diffraction spectra seen at the back of the objective are well defined, the longer wave lengths (the most diffracted) being outside the cone of rays grasped by the objective. This phenomenon is fairly commonly noted in microscopic studies of fine structures and a fuller treatment of it will be presented in a later paper.

[6] Proc. Manchester Lit. and Phil. Soc. **3**, 198 (1864).

[7] Mallock (*loc. cit*) has called attention to this.

[8] The angle at which this spectrum is diffracted can be roughly measured and the "grating space" calculated from it, with a fair approximation to the interval between the striae as measured microscopically.

[9] Onslow: *loc. cit.* p. 11.

Selective reflection (surface color) has been thought to be the cause of iridescence in insects. Walter,[1] who saw "*Oberflächenfarben*" in almost every case of iridescence in nature, failed to reconcile this hypothesis with many of the well-known properties of the objects to which he applied it. Iridescent scales have many such points of difference: sensitiveness to pressure or crushing,[2] resistance to bleaching or extraction,[3] loss of color or permeation with liquids and restoration on drying,[4] transmission color much less saturated than reflection color,[5] highly complicated mingling of hues,[6] very marked change of reflection and transmission colors with angle of incidence.[7] These discrepancies parallel those emphasized by the present writer in eliminating selective reflection from the possible causes of iridescence in feathers. Moreover, it must be borne in mind that the polarization effects and metallic lustre,[8] and the brilliant colors[9] exhibited by selectively reflecting substances are very similar to those of thin films. Süffert,[10] is an admirably scientific study, has assembled the properties of the various types of color possible in iridescent butterfly scales, and concludes very positively against the "surface color" theory. If it were only supported by Walter, it would probably have ceased to trouble people; but Michelson's paper[11] gave it a new lease of life.

He starts out with the statement that interference colors are "so rare and so readily distinguished from the true metallic [surface] colors that they may be most conveniently treated as exceptions after the subject of surface color has been considered," yet the chief characteristics by which metallic reflexion may be distinguished are as follows:

"1—The brightness of the reflected light is always a large fraction of the incident light, varying from 50 percent to nearly 100 percent.

"2—The absorption is so intense that metal films are quite opaque even when their thickness is less than a thousandth of a millimeter.

"3—If the absorption varies with color, that color which is most copiously transmitted will be part of the incident white light which is least reflected—so that the transmitted light is complementary to the reflected.

"4—The change of color of the reflected light . . . follows the invariable rule that the color always approaches the violet end of the spectrum as the incidence increases."

As Onslow has shown by quantitative measurements, and as anyone may observe for himself in a qualitative way, thin films, especially multiple films satisfy the first criterion. Michelson has admitted that the natural iridescent

[1] *loc. cit.*

[2] Mallock and others.

[3] Urech: Z. wiss. Zool., **57**, 306 (1894); Bayliss: Entomologist, **57**, 52 (1924); Coste: **23**, **24** (1890-91); and others.

[4] Biedermann, Bayliss, and others.

[5] Biedermann: *loc. cit.* Rayleigh: Phil. Mag., (6) **37**, 98 (1919).

[6] Coste, Rayleigh.

[7] Rayleigh.

[8] Mason: *loc. cit.* p. 437.

[9] Onslow: *loc. cit.* p. 27.

[10] *loc. cit.*

[11] *loc. cit.*

colors "are far more vivid than any of the reflexion hues of aniline dyes, or any other case of 'surface color' yet discovered." Rayleigh has taken issue with him on the second count, pointing out that the transmission colors of the insect scales are very much less saturated than those of dyestuffs, while the reverse is true of the respective reflection colors. In the single instance where Michelson tried to penetrate an insect scale by liquid he notes that the iridescence was completely destroyed if the index of refraction was between 1.5 and 1.6, and admits that selective reflection is ruled out in this particular case. As many investigators have noted, this loss of color on penetration appears to be without exception in the case of the iridescent insect scales. Rayleigh also points out that the third criterion is only roughly correct, and it is well known that more than one type of structural color shows complementary reflection and transmission. He also emphasizes that "with ordinary unpolarized light the surface colors appear to change too little" with changing incidence, and concludes that "Michelson's four tests are as well if not better borne by an interference theory." The present Lord Rayleigh[1] and Mason[2] have pointed out exceptions to the statement regarding the invariable change toward violet with increasing incidence.

Michelson's quantitative study of the "phase differences" and "amplitude ratios" of the elliptically polarized light reflected from dyestuffs and from "metallic" insects and feathers shows fair agreement. But the surfaces of the latter specimens are highly complex, as he admits, and the measurements have not been made on any types of structural color for comparison, though thin films are known to polarize light elliptically, and to behave similarly to surface colors with polarized light,[3] and since his "metallic" feathers turned out to have thin-film colors, this phase of the evidence can not be taken too seriously. The present Lord Rayleigh has been able, by means of spectrometric examinations, to obtain data showing that some of the beetles which were Michelson's best examples of surface color exhibit optical behavior corresponding to that of multiple thin films. Merritt[4] has made some more recent spectrophotometric studies on feathers and butterfly scales which show good agreement with the properties of thin films. Keeley[5] came to a similar conclusion as a result of his work with the microspectroscope.

As far as qualitative tests go the evidence is certainly against the "selective reflection" theory, and the odds appear to be more than even on the quantitative side as well.

The various other theories which have been advanced to explain the iridescence of insect scales are of minor importance. Resonance has been suggested by Wood.[6] Kossonogoff[7] assumes that all the colors of *Lepidoptera* are due

[1] Proc. Roy. Soc., **103A**, 233 (1923).
[2] *loc. cit.*
[3] Mason: *loc. cit.*
[4] J. Opt. Soc. America, **11**, 93 (1925).
[5] Proc. Phil. Acad. Nat. Sci., **63**, 112 (1911).
[6] Phil. Mag., (6) **38**, 98 (1919).
[7] Physik. Z., **4**, 208, 258 (1903).

to the resonating properties of fine pigment granules in their scales and Chirvinski[1] elaborates this theory. Such an all-inclusive explanation leaves us no better off than before, while resonance of the sort Wood observed with his granular metal films is subject to the same objections as selective reflection, of which it is a special case.

Studies of Typical Iridescent Scales

It will be seen from the studies of typical specimens which follow that their properties are, as indicated above, markedly at variance with those of diffraction or selective reflection colors. Positive evidence in favor of another explanation will be presented later.

The specimens were first examined with the naked eye, both with diffuse and unidirectional light at varying angles of incidence and falling crosswise and lengthwise of the scales. The inclination, curvature, and arrangement of the scales on the insect were observed with a Greenough-type binocular microscope to which was attached an orienting device so that a variety of relative positions of the scales, wing, illumination and observer were possible. Scales were removed from the specimen by scraping or by picking up on a cover glass slightly sticky with a film of balsam or glucose. This afforded an easy method of observing several scales at one time, and of studying their under surfaces. The reflecting properties of the scales were observed under inclined illumination, and also by means of a vertical illuminator fitted with a movable reflector so that the incidence of the illuminating beam could be varied within the angular cone of the objective. An iris diaphragm stop in the objective enabled its aperture to be reduced so that the light was almost wholly vertical rather than convergent. Reflection, transmission, and polarization at various orientations could be observed systematically by means of a Fuess petrographic microscope with theodolite stage.

For detailed study of the fine structures of the scales a number of different objectives, including those of 1.40 N.A. were available, and it was found that a fairly adequate idea of the cross-section and the interior of the scales could be formed by careful focussing of a lens of the appropriate aperture ("optical sectioning") and by proper manipulation of the condensor to furnish axial or oblique illumination. The interpretation of appearances by such a procedure was substantially in agreement with that obtained from study of the sections, in cases where these were available for comparison. In this phase of the investigation Onslow's observations can hardly be surpassed; his paper gives excellent figures of sections of a large number of scales, but, as Süffert says, a clear understanding of the general structure of the scale should precede a study of its cross-section. The latter is useful mainly for relatively large details and as a confirmation; the minute structures may often be revealed quite as usefully in torn or crumpled scales. Fracture, behavior under compression, and the process of slow permeation by viscous liquids are of great value in forming a concept of the object which is under examination.

[1] Russ. Ent. Rev., **15**, 513 (1915).

Since the structures concerned in the production of color are practically at the limit of resolution, even under favorable conditions, it is obvious that optical tests are likely to be more significant in establishing the nature of the observed phenomena. The conclusions drawn from such tests should of course be compatible with any structural conditions known to be present.

The behavior of iridescent scales in response to swelling agents is noteworthy, and is best brought out by exposure to phenol vapor,[1] since this does not wet the scale, and is readily removed by exposure to the air. Ammonia water, alcohol, and many other liquids have considerable swelling action also.

A series of practically colorless liquids, varying in index of refraction from 1.33 to 1.8, enables the scale to be surrounded or permeated by media of a wide range of refractivity. Liquids of different degrees of volatility (water, alcohol, benzene, xylene, etc) are useful in the study of the surface and internal structure of the scale as these are exposed by the evaporation of the liquid in which it has been immersed.

Bleaching, where necessary to eliminate the effect of pigment or to establish its absence, is best carried out with concentrated hydrogen peroxide (10-30%).

Urania and Similar Scales

Urania (*Chrysiridia*) *ripheus* is perhaps the most striking of all the iridescent scale-bearing insects, both because of its brilliancy and its variegated hues. The fore wings are blue green, changing to violet at grazing incidence, and the hind wings are a bronze green shading into reddish purple. The under surface of the hind wings presents a number of hues. At their roots they are brilliant bluish green, and vary in a distance of 5 mm. through blue, purple, and red to orange. The main area of the under side of the hind wing is greenish brass-yellow, in the center of this space the color varies through orange to red. The above colors are described as seen at normal incidence. Their distribution most closely resembles the zones of color seen when oil is spilled on wet asphalt pavement.

Structural Features. The iridescent scales are square-ended, strongly convex about their transverse axis at the outer extremity, so that on the wing the surfaces exposed are highly curved. Detailed study of scales from the different colored areas reveals no observable structural difference. Separate scales are longitudinally striated on their upper surface, the striae being really thin vanes, separated by spaces four or five times their thickness, the under surface is practically smooth. Transmitted light reveals, in addition to the longitudinal striations, a faint irregular tracing which appears to be inside the scale, and is probably the residue of the scale contents. Broken or crumpled scales permit the vaned structure to be recognized as part of the upper lamina of the scale, the lower lamina appears thicker (*ca.* 2μ) and in close contact with the upper one. Edges of torn fragments indicate a cleavage in the plane of the scale. The individual lamellae are not sharply defined, but the broken

[1] Wilson [(Psyche. No. 75 (1880)] noted that an insect packed in a box with phenol on cotton, and sent to be painted had its color changed from rich purple to green; fortunately for the picture a short exposure to the air was sufficient to restore the original hue.

edge resembles a torn group of sheets of paper, and buckling of the scale may cause them to separate somewhat. This lamellar structure is undoubtedly existent, though composed of films too thin to be visible even in Onslow's excellent sections. There are probably between five and ten lamellae present. Accurate observation of their individual thickness and that of the space between them is excluded by the limitations of resolving power of the microscope and the technique of sectioning.

Optical Features. As they lie on the wing, the scales show high reflecting power, through a considerable angle, but examination under the Greenough binocular microscope shows that the reflection is strictly specular, and the convex surface of the scale permits some part to be in position to reflect through considerable variation in the inclination of the wing. The reflecting power is high, and the lustre is metallic, apparently nearly as bright as polished copper in the case of the red scales. The reflection comes from spaces between the vanes. Lustre and specularity of reflection are even more marked on the smooth under surface of the scale. Torn or split scales show that the reflections come from the lower lamina, and the very thin upper lamina with its vanes acts only as a screen thru which these reflections are observed. Under fairly diffuse illumination the reflection color of the scale is not uniform, but varies markedly from center to tip. This is due to the different inclination of these different portions of its surface, for when the scale is flattened, or when the angle of incidence is actually the same, the color is correspondingly uniform. The uniformity is not perfect, for slight local variations are apparent. These blend into the adjacent colors, and in no case are there marked differences in hue. The reflection colors are highly saturated and are localized in the lower lamina.

The transmission color is much less saturated and is tinged with the faint yellowish pigmentation of the scale. The hue varies from center to tip just as does the reflection color, and this variation is eliminated by flattening the scale or by tilting it so that the different portions of its surface are each successively observed with axial light. The transmission colors are complementary to the reflection colors, as shown by combined reflected and transmitted illumination.

As the angle of incidence is increased the hues of the reflection colors change very strikingly, this is much more marked in the individual scale than on the wing because of the multiple convex character of the latter, which permits a wide range in the angle of incidence and a consequent lessening of the purity of the colors and of the sharpness of their changes. The sequences from normal to grazing incidence are as follows:

green → blue → purple,
blue → purple → red → orange,
reddish purple → orange → yellow green.

Some scales, violet at normal incidence, go through reddish purple, copper red and orange yellow to greenish yellow, with increasing angle of incidence. The above changes in the reflection colors are accompanied by corresponding

changes in their complementary transmission colors. On the wing the joint effect of these color changes results in a *shifting* of the color zones. The bands of blue, purple, red, and orange move to the adjacent portion of the wing, while maintaining the same zonal distribution. This shift of location is toward the portion of the wing blue at normal incidence, and is due to each of the colors changing to ones following it in the above series.

When the change in hue of the reflection color is analyzed by a nicol prism, one notes that if the plane of vibration of the nicol is perpendicular to the plane of incidence of the light the color phenomena are practically the same as without it. If the plane of vibration of the nicol is parallel to the plane of incidence the reflection is practically destroyed at an angle of about 60° to the normal, and, at greater incidence than this, the color is complementary to that seen with the nicol in the perpendicular position or with it removed completely. If a "¼ undulation" mica plate is inserted, the plane of the nicol being parallel to the plane of incidence, the color undergoes a complementary change.

Between crossed nicols the scales are seen to be anisotropic, with extinction parallel to their longitudinal striae. This is purely structural anisotropy, for it is destroyed when the scale is rendered optically homogeneous by permeation by a liquid of the same refractive index as chitin. Any reflecting or refracting surface tends to depolarize light; multiple surfaces, such as the grooves of a deeply ruled diffraction grating exhibit this effect and the parallel ridges of the scale undoubtedly act in a similar manner.[1] The anisotropy is not sufficient to interfere with the observation of the elliptical polarization of the reflected light described above, for this may be observed with the scale in any azimuth, and depends only on the angle of incidence.

The distribution of colors on the individual scale, as mentioned above, is not perfectly uniform; a given hue such as red may show variations toward adjacent colors, such as purple or orange. These variations are gradual, though they may take place in a distance of only a few microns. The complementary color shows similar variations, though these are much less marked because of its low saturation.

Pressure applied to a scale causes a very marked change in its hue. This may be carried out under objectives of fairly short working distance by wedging a spear-pointed dissecting needle between the mount of the objective and the cover glass. Transmitted or reflected light may be used for observation. Very slight pressure is sufficient to alter the color to an adjacent one, and increased pressure brings about a succession of colors similar to the sequence seen with increasing angle of incidence. Extreme compression destroys all but the faint yellow pigment color. Unless the scale is actually disrupted the original color is restored on removal of the pressure, particularly if the atmosphere is moist.

Under the microscope the effect of pressure may be seen summarized on a single scale which has been bruised locally by a dissecting needle or com-

[1] Ambronn [(Kolloid-Z., 6, 222 (1910)] has termed this phenomenon "rod double-refraction."

pressed only at one end. The whole series of reflection and the transmission colors is present in a space of a few microns. Yellow-green scales are altered through green and blue to purple by reflected light (more severe pressure disrupts the scale and destroys the color); the transmission color goes through purple and red to orange, and is finally lost in the yellow of the pigment. Red-purple scales go through red and orange to yellow, or yellow green, the complementary transmission color, bluish-green, is lost with moderate pressure and only the yellow of the pigment is seen.

Swelling the scales is carried out by exposure to phenol vapor, ammonia or even water vapor. Here again the color changes very strikingly and in a sequence the reverse of that caused by compression. The original color is restored on exposure to the air.

Penetration by liquids affords the most convincing proof of the structural nature of the colors of the scales, for if the liquid is of index of refraction substantially the same as that of the scale (as determined by the Becke test)[1] the reflection color is completely destroyed, and only the transmission color of the pale yellow pigment remains. The original color is perfectly restored on removal of the penetrating liquid. If the index of refraction of the chitin is not perfectly matched, the loss of color is not complete, though with liquids of n between 1.5 and 1.6 it is very nearly so. With liquids of index of refraction widely different from that of chitin, the intensity of the reflection and transmission colors is decreased, and in addition their hues are altered. This alteration results in green scales becoming red, and may be due to the swelling action of the liquid, (which would cause a change of this nature) or to the replacement of the air in the voids of the scale by a medium of higher refractive index. Certainly the former plays a considerable part in this color change for one notes under the microscope that the *saturation* of the color may be restored by replacement of the liquid by air, but the original *hue* is regained only after a few seconds further drying to remove the swelling liquid in the scale tissues themselves.

The progress of the penetrating liquid may be followed under the microscope, if liquids of high viscosity (balsam or glucose) are used, and it is seen that the liquid enters most readily at breaks in the scale, spreading through it independently of the striations or other markings. If only the outside of the scale is wetted no loss in color results.

When the permeating liquid is allowed to dry out slowly the vaned surface is first exposed, and at this stage the scale is still colorless. On further drying, flashes of color appear over areas in various parts of the scale, and these colors apparently become more saturated with succeeding overlapping flashes until finally the original saturation of color is restored. This spreading of the color throughout the scale is independent of its striae, and is similar in appearance from either surface.

The optical properties of other *Uranidae* are closely similar to those of *U. ripheus*, with minor differences as regards the hues present. Bronze-green,

[1] Johannsen: "Manual of Petrographic Methods," 271, (1918).

changing to blue or purple at grazing incidence and to copper red on swelling, is their most prevalent color. The changes on compression are very striking, on a single scale one may see absence of color where the pressure has been most severe, and transmission colors of yellow, orange, red, purple and blue in order outward from this point, with a corresponding complementary series of reflection colors. The parallelism between the variation of both reflection and transmission colors with pressure and with increasing incidence is highly perfect.[1]

Ino statices has iridescent scales of the same general type as those of the *Uranidae*, but differing from them in certain structural features. Their bronze-green color is localized in the upper lamina of the scales, and shows specular reflections, change with pressure, swelling, or varying incidence. However, the longitudinal corrugations of the upper lamina, instead of being fairly smooth ridges, are studded with rows of raised bosses. The sides as well as the tops of these reflect specularly and evidently this is simply a special case of a very highly "embossed" upper lamina, similar in other respects to that of the scales just described.

Papilio peranthus shows the converse of the above structure, with longitudinal ridges, unevenly spaced cross ridges connecting these, and depressions in the space between these raised structures. Süffert aptly compares the surface to that of a waffle. The reflection is specular from all parts of this embossed surface, just as in *Ino statices*. The under surface of the scales shows the reverse of these depressions as elevations, though the reflection is hardly as brilliant.

Many iridescent butterflies exhibit optical properties very similar to those of the *Uranidae*. The scales of *Papilio philenor* contain a dark pigment localized in their upper lamina, which is relatively thick, with shallow longitudinal ribbing. They show the color changes with inclination, pressure, swelling and penetration as do the scales of the *Uranidae*, but the pigmentation suppresses the clearness of these phenomena somewhat, particularly on the upper surface of the wing. The lower lamina is iridescent, independent of the upper one. Because of its less pigmentation and unstriated surface it is rather more brilliant. A lamellar structure is indicated by the character of torn and crumpled edges, and the lamellae of the upper lamina follow the ridges of its surface. *Papilio asterias* exhibits much less perfect color producing scales, with hardly perceptible iridescence or metallic lustre. It is more heavily pigmented, and the striated and cross-marked upper lamina constitutes a screen which practically conceals the iridescence of the lower lamina.[2]

Papilio neophilus olivencius has a similar mesh structure on the upper surface of the scales, which gives them a matte lustre. The seat of the

[1] The foregoing observations are very similar to those made by Süffert, who considers the scales of *Uranidae* as a type example. The colored plates of his paper represent the above variations in hue very vividly.

[2] Such a structure is similar to that found in many scales not thought of as iridescent, in which the relatively opaque and heavily sculptured upper lamina conceals the lightly pigmented, highly iridescent lower lamina. The under side of the black scales of *Urania ripheus* shows brilliant iridescence. Indeed, iridescent lower laminae are very common in the scales of moths and butterflies, whether the scales are iridescent or not as seen on the insect.

iridescence is beneath this layer, and is very brilliant from the under side of the scale. The scales of *P. nireus* and *P. zalmoxis* are essentially similar.

Callimorpha dominula is much the same as the preceding specimens, having a heavily pigmented, non-iridescent upper lamina, which masks most of the iridescence of the thin, unpigmented lower membrane.

Lycaena icarus, a common European butterfly, is a bright lavender; the wing appears light gray at grazing incidence. The inclination of the scales on the wing is partly the cause of this, but another factor is more important.

The almost complete loss of iridescent color at large angles of incidence is due chiefly to the character of the upper lamella of the scales. This is longitudinally striated, the striae being connected at short intervals by a fine cross-structure, making a mesh pattern which is relatively thick. The openings of this mesh are large enough so that the iridescence of the lower lamella is visible through them at small angles of incidence, but as the angle approaches grazing, the iridescence is hidden behind the edges of this boldly sculptured structure. As far as can be observed under these circumstances, the optical properties of the scales parallel those of the specimens already described. Pressure causes a marked alteration of the color of the scales, but since they are very thin, Newton's rings may be seen between the slide and the cover glass in their vicinity, and these colors are likely to be confusing. Very sudden release of the pressure destroys the Newton's rings before the scale has time to recover its original hue.

The lavender color is completely destroyed on penetrating with a liquid of $n = 1.5 - 1.6$ and, on drying out, an interesting sequence of changes is noted. When the outer surface of the scale emerges from the liquid, its raised striations produce a blue transmission color, as seen with an objective and condensor of the proper aperture.[1] Then the liquid in the underlying tissues is gradually replaced by air, and the yellow transmission and lavender reflection colors are restored. The scales of *Lycaena corydon* are substantially the same as those of *L. icarus*, but more closely striated and less lustrous. *Basilarchia astyanax* has scales similar in structure to those of the *Lycaenae*, with a "mesh" upper structure and an iridescent lower lamina, the colors of which are ordinarily seen through the openings of the mesh. *Cercyonis alope* is similar, but much more pigmented, with iridescence visible only under brilliant illumination.

The genus *Anaea* contains some good examples of iridescence similar to that of the *Urania* moths. *A-morvus* is particularly noteworthy for the great change which its colors undergo on exposure to phenol vapor. Light greenish blue at first, it changes through bronze green, orange and copper red, to purple with maximum swelling, and passes through this series in the reverse direction in a few minutes when exposed to the air. The same reversed sequence is noted as the angle of incidence goes toward grazing, though this is not so easily observable on account of the inclination of the scales on the wing, and because the upper lamina possesses a "mesh" structure similar to that of *Lycaenae*.

[1] See page 327, footnote 5.

Helicopis cupido and *Argynnis* ("Silverspot") are examples of another sort of scale color, of the same type as that of *Uranidae*. Their scales are pigmentless, and give a general effect of white on the wing, with bright silvery lustre microscopically. Rather pale iridescent colorings are observable by reflected light, and less saturated, complementary ones by transmitted light. The coloring is not uniform, and the various hues blend into each other giving an appearance much like mother-of-pearl. The behavior with pressure or when penetrated by liquids is closely similar to that shown by the insects described in the preceding studies. The specularity of reflection is another point of resemblance.

Cocytia durvilli has iridescent body and leg scales which are of the same general type as the others just described. Their elongated character adds to the satiny lustre as seen on the insect.

Of more primitive forms, *Eriocrania* (*purpurella*?) shows scales having a very simple structure, consisting apparently of a simple basal membrane bearing longitudinal ridges or vanes. This behaves as if it were a single thin film with no interior air space. The reflection color (purplish to orange) is relatively faint, and is lost if either the upper or lower surface of the scale is in contact with liquid.

The foregoing specimens have all been essentially similar as regards the color-producing portion of the scale, and their differences lie chiefly in the various means by which the action of this structure is modified by other portions of the scale. The seat of the iridescence, in the above cases, may be in either lamina of the scale; the upper lamina may vary from a simple vaned film overlying the reflecting structure to a pigmented mesh structure in high relief. The reflecting plane is parallel to the plane of the scale.

The scales of *Ornithoptera* are somewhat different from those just described, but may well be classified with them; *O. poseidon* is a typical example.[1] Its wings exhibit only moderate color change with angle varying from somewhat yellowish green to blue-green. At grazing incidence an orange-red sheen is visible in certain azimuths.

Structural Features. The scales themselves are nearly oval, highly convex, and over-lap on the wing very closely. They are uniform in thickness, and much less flexible and fragile than the scales previously studied. No coarse striation or mesh structure is present, but with high powers very fine and regular striations (about 1 μ between centers) are visible on the upper surface of the scale.

By transmitted light the structure appears to be simple, a plate of slightly turbid chitin with a finely striated upper surface; by reflected light it is seen that the body of the scale is not optically homogeneous but shows a fine stippling of reflection color. This is independent of the striations, and is visible from either surface of the scale. It is distinctly beneath the striated surface. Individual bright points of this stippled coloring appear to show something approaching specular reflection.

[1] Dr. Forbes points out that it is rather surprising that *Papilio philenor*, which is really one of the *Ornithoptera*, should have scales so different from the other members of this genus.

Fractured or distorted scales show little tendency to cleavage along the striations, and these cannot be isolated or flattened sidewise. There is little indication of a cleavage in the plane of the scale, but the edges of the fractures show some evidence of a lamellar structure.

Cross sections show that the striae are closely packed, between 1 and 2 μ high, and might equally well be thought of as a system of fine parallel grooves in the upper surface of the scale. The body of the scale appears rather more turbid than the upper or lower portions, but the differentiation between the cuticle and the interior is not very pronounced under the microscope. Oblique, broken, or distorted sections show distinct evidence of a laminated structure which apparently extends throughout the interior of the scale, parallel to the surface. This portion is not visible if the section is penetrated by a liquid, but on evaporation and entry of air, its opacity increases.

Optical Features. The most distinctive characteristic of the scales of *Ornithoptera* is the absence of true specular reflection. The scales show "high lights," but these are not sharply defined, and there is obviously a certain amount of diffuse reflection. Because of this, their lustre is hardly metallic, and their coloring less bright than that of the *Urania* scales. On the other hand, the color is visible over a wider angle. The reflection from either surface of the scale is essentially the same, for the striae are hardly visible except by transmitted light. On focusing up and down through the scale with an objective of very low "penetrating power" the reflecting surface cannot be definitely located; instead, reflection appears to take place from any level. This is borne out by study of the under side of the scale.

The reflection coloring of the scales is matte rather than metallic; yellowish green predominates, and the scales are remarkably uniform in hue. They are strongly colored by a non-granular yellow pigment, and this undoubtedly modifies both the reflection and the transmission colors. By transmitted light the scales are orange pink.

The orange-pink transmission color is what is seen at grazing incidence when the scales are on the wing. This may be studied under the binocular microscope and the various reflections and transmissions of the light by the overlapping scales may be clearly seen. The convexity of the scales is a considerable factor in the "reflection" of their transmission color, for light may be totally reflected at the lower surface of the scale, and travel a considerable distance in it before emerging. It is also noted that the orange sheen is greatest when light falls across the striations of the scales as the lie parallel on the wing. Here the yellow striae, which project above the portion of the scale where the green color originates, present an ideal finely divided transparent medium to scatter and to color the light which falls across them. Moreover, the curvature of the surface is greater crosswise. No orange sheen is observed on the *under* surface of scales stripped from the wing as a group. Their reflection color is green (instead of yellowish green), changing to violet at grazing incidence. If the scales on the wing are surrounded (but not penetrated) by a liquid their surface reflection is minimized, and the color from the interior shows up clearly at any angle, with none of the orange sheen.

The color of the scale varies with the angle of incidence, the reflected yellowish green changing toward blue and the transmitted orange-pink toward yellow. Polarization effects cannot be observed distinctly on account of the scattering of the reflected light.

Swelling reagents cause less alteration in the color than in the case of the *Uranidae*. The green becomes more yellowish, and the transmission color becomes more pink. These changes are reversed on exposure to the air.

Pressure brings about a very distinct change in the reflection color, from green through blue to reddish purple, before it is finally destroyed. The transmission color loses its pink and finally only the yellow of the pigment remains. Removal of the pressure with exposure to a moist atmosphere is sufficient to restore the original hue. Pressure on swelled scales first restores their original color and then alters it as indicated above.

Penetration by liquids is not so rapid as in *Urania* scales; the scale may lie completely immersed in liquid for some minutes before it is affected, though broken scales are more rapidly permeated. With a liquid of index of refraction near that of chitin (1.5 – 1.6) the iridescent color is perfectly destroyed and only the yellow pigment color remains. Removal of the liquid restores the original coloring. (Most liquids have a certain amount of swelling action, judging from the "lag" between the restoration of color and lustre, and the recovery of the original hue.)

The progress of penetration by liquids is similar to that in *Uranidae*, and is independent of the striae. The loss of color is gradual and more or less by stages, a given spot on the scale appearing less and less green until all its reflection color is lost. On evaporation of the liquid, irregular patches of faint color first appear, and, as these extend throughout the scale, successive additional patches of color appear, developing over the areas already colored; finally the original saturation of hue and intensity of lustre is completely restored.

Morpho and Similar Scales

In a number of respects the iridescent scales of the well known family of *Morphos* are different from those of the insects just described. A brilliant, highly metallic blue is the prevailing color, and this is present only on the upper surfaces of the wings. The variation in hue with change in angle of incidence is easily observed, reddish purple being the extreme color noted. The reflection colors are seen best looking from the base toward the tip of the wing ("with the grain" of the scales). This is only partly due to the inclination of the scales on the wing.

Structural Features. The scales of the *Morphos* are practically plane, and lie close to the wing, like shingles on a roof. *M. menelaus* has a double layer of iridescent scales. The outer ones are very thin, long, and narrow, shaped like the blade of a paddle, with longitudinal striae rather far apart (*ca.* 1.5-2μ) and standing up like vanes on the upper lamella of the scale. Broken or crushed scales show these vanes flattened or torn loose from the scale proper, while scales folded crosswise permit their elevation to be seen; they are from 2 to 3 μ high. The vanes usually break cleanly, but may give evidence of a

longitudinal "cleavage" slanting very gradually from the upper edge to the base. There is no indication of a hollow interior in the scale.

Optical Features. On account of their great transparency the outer scales are best studied after being removed from the wing. On examining them by reflected light with a 4 mm. objective, it is evident that the vanes are the seat of the color, and that the laminae of the scale do not contribute to its iridescence. The reflection consequently is not specular from the surface of the scale as a whole, but is so from the upper edges of the vanes.

Torn or split scales, in which the vanes are loosened or removed from the lamina of the scale afford convincing proof of this; a single, isolated vane shows just as brilliant reflection and color as when in its normal position on the scale. However, with axial illumination and an objective of narrow aperture, no reflection is noted even though the plane of the scale is perpendicular to the illuminating beam. It is only when markedly oblique illumination is supplied that light is reflected up along the axis of the microscope. Evidently *the reflecting structure is not parallel to the plane of the scale.* This may be confirmed by tilting the scale until it reflects along the axis of the microscope with vertical illumination, or by rotating the stage in the plane of the scale after the illumination has been adjusted to such an obliquity as to be reflected along the axis of the microscope. In the latter case the vanes appear bright only once in a revolution; this behavior corresponds to the "oriented lustre" of etched metal specimens, and of laboradorite, cats-eye and similar minerals, all of which possess systematically arranged reflecting surfaces oblique to their own general surface.

The plane of reflection by the above tests is found to "dip" toward the root of the scale, making an angle of between 10° and 20° with its laminae and with the edges of the vanes. Since there is practically no reflection from vanes flattened in the plane of the scale, it appears that the tilting of the reflecting structure is only lengthwise of the scale, and that it passes through the vanes rather than following up one side, over the upper edge, and down the other side.

The "dip" of the reflecting plane in the vanes is the equivalent of tilting the scale on the wing, so that although the scales of the *Morphos* lie nearly flat, the reflection from the wing surface is that corresponding to markedly inclined scales. The intensity of the reflection is very marked, the narrow edge-views of the vanes appearing as highly luminous blue lines.

The iridescent color is obviously of structural origin and connected with the peculiar reflecting properties of the individual vanes, since it shows its full intensity on an isolated vane or on vanes which have been twisted laterally, and does not depend on their arrangement or proximity to other vanes on the scale. The color changes with angle from greenish blue for illumination normal to the reflecting plane to purplish red at grazing. If the color change is referred to this plane, it is consistent for all azimuths, but if referred to the plane of the scale the behavior is not so simply described.

As seen by reflected light, the edges of the vanes are not clear lines of blue, but each one is crossed, at intervals of 1-2 μ or more, by fine dark markings, which give them a somewhat "beaded" appearance.

By transmitted light the scales are seen to be unpigmented, and only faintly yellow along the color-producing vanes.[1]

Polarization effects comparable to those shown by *Urania* and other similar insects are not to be observed accurately on account of the complexity of the surface of the scales, and the strong possibility of interference by polarization from its deeply ribbed structure.

Between crossed nicol prisms the scales are seen to be anisotropic with parallel extinction; this is purely a structural phenomenon, since it is destroyed by permeation of the scale with liquid of the proper refractive index. The anisotropy is localized in the vanes, a single isolated one showing it fully. When the vanes are flattened by pressure or distortion of the scale they are only faintly anisotropic. The extinction shown by the vanes seen flatwise is not sharp, on account of the weakness of their polarization color, but is apparently parallel or of small obliquity.

With one nicol the scales may show an apparent pleochroism, blue for vibrations parallel to their vanes, and greenish for transverse vibrations. This is related to the diffraction color described on page 327 (footnote 5). The blue is at a maximum for vibrations parallel to the diffracting structure; diffraction is at a minimum for vibrations perpendicular to this direction, and the blue, lessened in intensity and combined with the pale yellow transmission color, appears greenish.

The reflection colors of the scales are less variegated than are those of the insects studied previously, though tints of green and purple may be seen mingled with the blue; a single vane may show slight non-uniformity of hue in different parts.

Pressure may flatten the vanes sidewise, destroying their reflection, but if this does not occur the hue is seen to be altered through dark blue and violet to reddish purple. It may be restored by exposure to a moist atmosphere.

Swelling the scales with phenol vapor causes the hue to change to yellowish green (going to violet at grazing). The original coloring is restored on exposure to the air.

Penetration by liquids of index of refraction close to that of chitin (1.5-1.6) results in complete loss of color. The original color is perfectly restored on removal of the penetrating liquid. Liquids of refractive index markedly lower than that of chitin cut down the reflection color somewhat, and alter its hue to yellowish green, which is due partly to swelling, and perhaps also to the replacement of air in the scale by a medium of higher refractive index. Wetting of the under lamina of the scale by the liquid does not alter the color, this occurs only when the liquid penetrates between the vanes and wets them thoroughly. On evaporation of the permeating fluid the color only reappears

[1] Onslow was disturbed by the fact that the scales may appear blue both by reflected and by transmitted light, but the latter is true only with objectives and illumination of the proper relative aperture, and is due to the causes indicated above (page 327, footnote 5).

after the vanes have been exposed, there is frequently an appreciable time interval after their exposure before the color develops in each vane separately.

The under scales of the upper surface of the wings of *M. menelaus* are superficially different from the transparent outer scales, but are similar in all important features.

Structural Features. The scales are flat and broad with blunt, uneven ends, and are very closely striated longitudinally. These striae are really fine vanes, as in the outer scales, so closely spaced as to be practically in contact, with no space visible between them. They are less than 1 μ between centers, though not perfectly even or parallel, and project about 2-3μ above the upper lamella. They may extend slightly beyond the tip of the scale. Fractured scales show that the vanes and upper lamina constitute the greater portion of the scale, and that the lower lamina is a simple thin membrane. Fractures tend to follow the vanes, giving the scales a well defined longitudinal cleavage. On account of their close packing, the fracture of the individual vanes is not readily studied, nor are they easily flattened sidewise.

Optical Features. The reflections from the scale originate in the individual vanes, and are seen only when these are in their normal position, perpendicular to the plane of the scale. A single isolated vane exhibits the full color and lustre. The reflecting plane is not parallel to the edge of the vane and in the plane of the scale, but is inclined to these, dipping toward the root of the scale at an angle of between 10° and 20°. With respect to this plane, the reflection is specular enough so that it is observed through a narrow angle only for any given angle of incidence.

In contrast to the outer scales, the under ones are pigmented fairly heavily, with a dull brown pigment, which is dilute in the lower lamina and is mostly in fine granules along the lines of the vanes. Since the scales are dark from the under side, it is evident that the pigment is mainly beneath the vane.

The under scales show color changes with varying angles of incidence precisely similar to those exhibited by the outer scales. Their polarization effects by reflected light are not well defined. Between crossed nicols they show anisotropy of structural origin, with parallel extinction, flattened vanes seem to show slightly oblique extinction.

On account of the close proximity of the vanes on the scale, pressure can be very effectively employed without flattening them sidewise, and the sequence of color changes from the normal light greenish blue to purplish red is easily observable. Their behavior on swelling is the same as that of the outer scales.

Penetration by liquids reveals the presence of a spongy interior, to which the thick, pigmented upper lamina with vanes is attached. Pressure on the empty scale forces air out of the interior and bubbles may be seen in the surrounding liquid, or if the scale is filled but not surrounded by liquid, this may be squeezed out as from a sponge. The scale possesses a considerable amount of elasticity. On drying out, the vanes are cleared of liquid first, and their color is restored. At the same time, or immediately after, the spongy interior empties, and the opacity of the scale increases further. The restoration

of the color on drying is along the vanes, as is its destruction on penetration. The condition of the interior of the scale or of the lower lamina does not govern the appearance of the color. The lower lamina has a slightly wavy surface, and is iridescent from either above or below. It is similar to the iridescent lower laminae possessed by nearly all butterfly scales, and plays no part in the color of the scales on the insect.

The scales of *Morpho sulkowskyi* ("Pearl Morpho") have practically the same optical properties and structural features as those of *M. menelaus*. The pigmented scales are a deep brownish orange by transmitted light but this is not all due to pigment, for penetration by a liquid of $n = 1.55$ destroys all transmission color but a weak grayish brown. Pressure also destroys much of the color. This dark orange transmission color is related to the blue reflection color, for it develops simultaneously with it as the permeated scale dries out.

The scales are distinctly pleochroic, from dark orange for vibrations crosswise of the vanes to lighter orange for vibrations parallel to them; this pleochroism is lost when the scale is penetrated by a liquid.

A number of other butterflies have scales which are similar in their optical properties to those of the *Morphos*. *Apatura* (*chlorippe*) *seraphina* is a widely studied example, which shows the vaned scales and inclined reflection typical of the insects just described. In the violet scales near the outer edge of the wing, the plane of reflection is distinctly more tilted than in the *Morphos*, and makes an angle of about 30° with the plane of the scale. The vanes of the scale, flattened sidewise, show oblique extinction, at an angle between 20 and 30°. The scales in the brilliant greenish blue band across the center of the wing have less inclined reflection, and their vanes do not show markedly oblique extinction when seen flatwise. *Apatura ilia* is similar in optical behavior to *A. seraphina*, but its colors are not as brilliant, possibly because of greater pigmentation; they range from greenish blue, to reddish purple at grazing incidence. The tilting of the reflecting plane, and the localization of the iridescence in the vanes are unmistakeable.

Ancyluris meliboeus is another insect having scales with iridescent and inclined reflection. It exhibits a very brilliant lustre, and colors similar to that of the *Morphos*, showing rather more variation in hue with increasing incidence, with pressure or with swelling. The reflecting plane makes an angle of 10°-20° with the plane of the scale.

Callicore eluina has scales showing practically identical properties with those of *Ancyluris meliboeus* as regards their hue and its changes with pressure, swelling or varying angle of incidence.

The *Morphos* and the specimens described after them constitute a second group with essentially similar optical and structural properties throughout. They are characterised by their vaned scales, the iridescence of which is localized in the individual vanes. The fact that their reflections do not originate in the plane of the scale but in a plane making an appreciable angle with it, is another distinctive feature. The lower lamina, though ridescent, is a negligible factor in the color of the insect.

The structural origin of the color and its changes with varying incidence, with pressure, and with swelling, are analogous to these properties as observed in the scales of *Urania* and other insects of similar nature.

Beetle Scales

The scale-bearing beetles have many points in common with the above moths and butterflies as regards their iridescence. *Entimus imperialis* ("Brazilian Diamond Beetle") is the best known of these, and is typical of them as a class.

Structural Features. The scales which line the pits in its integument are flat, paddle shaped or more elongated, with no ribbed or meshed structure. Their upper and lower surfaces appear structurally identical.

Fractured scales, or those torn by a fine needle show indications of a lamellar structure, the broken boundary is like the torn edge of several sheets of paper. Sections of the scales furnish little additional information. The "cuticle" of the scale is about 1 μ thick, and the interior of the scale is 4-6 μ in thickness. Both cuticle and scale contents appear practically void of structural details; the interior portion is not perfectly clear and glassy, but no direct evidence of a lamellar structure is apparent. In plan the scales show a very fine and rather indistinct pattern of lines, substantially equidistant, and more or less curved, resembling a portion of a finger print or lamellar "pearlite" in steel. The slightly curving lines may extend from edge to edge of the scale. and may run across it at any angle. On some scales there are sharply defined areas (coincident with the patches of various colors) in which the lines run in different directions.

Optical Features. Blue-green is the most common reflection color of the scales of *Entimus imperialis*, but some may show yellow-green or orange. These colors are very brilliant and lustrous, as seen from either surface of the scale; dark field illumination shows a certain amount of scattering of light by the interior of the scale. This results in a somewhat "opalescent" appearance, and the reflections instead of being strictly specular, may be spread through an appreciable angle. However, this scattering is slight, and the general effect is that of highly metallic lustre on the individual scales.

The plane of reflection is not always parallel to the principal plane of the scale, and may be inclined appreciably from it. This may be observed readily with axial illumination and axial observation as obtained by an objective with iris diaphragm and a vertical illuminator. The scale may be shown to be flat against the slide on which it rests, by the observation of the colors of Newton's rings between it and the glass. The tilting of the slide necessary in order that the scale shall reflect axial light back along the axis of the microscope may be measured; angles of 10° to 15° are not uncommon. This tilting of the reflecting plane is also evidenced by the swaying of the image with reflected light on focussing up and down. It may also be observed, with strictly vertical illumination, at the back aperture of the objective; the reflection color is seen to be markedly off center. Movement of the reflector in a mirror-type vertical illuminator, to furnish oblique reflected illumination also

demonstrates the inclination of the reflecting plane, particularly if the stage is rotated, when "oriented lustre" may be seen very strikingly.

When the scale is inclined to the axis of the microscope so that its reflecting plane is perpendicular to the axis, rotation of the stage reveals no "oriented lustre". With the scale more inclined to the axis, rotation *in its reflecting plane* causes no change in lustre or hue.

The anomalous reflecting properties described above are related to the structure and color of the scale; the different colored areas, in which the striations run in different directions, show inclined reflections which are sharply defined by their boundaries. The tilting is always *crosswise* of the striae, and is less where they are farther apart. With a scale half yellow and half green by reflected light, the yellow image sways in one direction while the green sways in another, on passing out of sharp focus. At the back aperture of the objective the green is seen to be at one side of the lens and the yellow at the other. In general the correlation between reflection, striation and reflection color is very distinct on these varicolored scales. When the color is uniform throughout, or only shows gradual variation in hue, the behavior is not so spectacular, but the inclined reflecting plane may be recognized in any of the scales where the striae are visible, and in most instances the angle of inclination is sufficient to prevent its being overlooked.

The reflection colors are uniform in hue in uninjured scales; a scale may be one color throughout or may be divided into areas of different colors. These areas are sharply defined, and constitute a "mosaic" of colors on the scales; ordinarily 2 to 5 patches of color are found on a single scale. The boundaries of these colored areas show no gradation of color, and are usually almost straight lines. Their outlines coincide with those of areas where the striations run in different directions, and where the reflection plane is tilted differently. Gradual variations in color are less common, but may frequently be noted in scales which have been altered by pressure. Pigment is wholly absent from the scales.

The reflection and transmission colors bear a complementary relationship to each other, and this is consistently true throughout the local variations in hue, so that the mosaic pattern is sharply defined either by transmitted or by reflected light. The reflection colors, brass-yellow, green, and blue, have respectively corresponding transmission colors of purplish blue, purplish red, and yellow. The transmission colors are very highly saturated. It sometimes happens that illumination with reflected light may reveal flashes of red, but this is really the transmission color seen by virtue of light reflected up through the scale from its under surface or from some surface beneath the scale itself.

The color of the scales changes with the angle of incidence to a marked degree. This may be observed either by tilting the scale, or by oblique illumination, either transmitted or reflected. With an objective of N. A 0.95 narrowing the aperture by means of a diaphragm changes the hue by cutting off the oblique rays and permitting only the axial portion of the cone to pass; this is particularly noticeable with transmitted light, and serves as a means of observing the pure color for one angle of incidence only. With axial trans-

mitted illumination the scale may be tilted and then revolved in its own plane; the transmission color does not change appreciably.

With increasing incidence the reflection colors pass from brass-yellow through green and blue to purple, and the corresponding transmission colors through purplish blue and red to orange or yellow.

The scales seen flatwise are isotropic between crossed nicols. Their reflection, analyzed by a nicol prism, shows the same behavior as *Urania* scales: at all angles of incidence, the same color for vibrations perpendicular to the plane of incidence as for unpolarized light; for angles greater than about 60°, complementary color for vibrations in the plane of incidence. Elliptical polarization is identified by means of a "¼ undulation" mica plate. The above tests are not easy to carry out, on account of the inclined reflecting plane, but the behavior is unmistakable when observed.

Since the scales have no prominent striations it is possible to test for any diffracting properties by illumination with a narrow cone of transmitted light; no diffraction spectra are visible in the back aperture of the objective, so no systematic ultramicroscopic structure of lines or dots is indicated. This is confirmed by unilateral (dark field) illumination. The colors are undiminished in diffuse light.

Pressure affects the coloring very strikingly. The patches of color tend to be rendered uniform in hue, and then the transmission color goes through purple, red and orange to yellow, and finally to colorless, the reflection color changes from brass-yellow through green, blue and reddish purple, to dark red and orange. The color is restored on standing a few minutes, or more rapidly by breathing on the scale.

Swelling also alters the color, in a sequence of hues the reverse of that passed through with increasing pressure. Exposure to the air restores the original coloring.

Penetration by liquids is significant, for it reveals the entire absence of pigment, and the structural nature of the coloring. With a liquid of $n = 1.55$ the reflection and transmission colors are destroyed completely. If the index of refraction is much greater or less than this value, the color is diminished in intensity but not wholly lost. The hue is altered somewhat, either because of swelling or because of the replacement of air by a more refractive medium. The original coloring is perfectly restored on removal of the liquid.

Liquids do not readily penetrate uninjured scales, but if they are torn or if their root affords an opening, the liquid enters and spreads rapidly throughout the interior. The process of penetration may be followed more easily if viscous liquids are used, and it is seen that the advancing front of the liquid is not a simple meniscus in the interior of the scale, but that it progresses in layers at different levels. The advance of these is practically even, but their fluctuations add to the appearance of a laminated interior. The loss of color coincides with the advance of the liquid in all levels; if only a part of these are permeated, the color is lessened but not destroyed. Where a boundary between two patches of color is encountered the penetration is momentarily interrupted, as if there were a break in the continuity of the voids through

which the liquid flows. The cuticle remains unaffected in the above process, and is evidently nothing more than a clear structureless membrane enclosing the interior of the scale, where the color is localized.

One of the most beautiful of the scale-bearing beetles, *Hadiomeas gemmifer*, has scales which are optically and structurally closely analogous to those of *Entimus imperialis*. They are mushroom shaped, with the root near the center of the lower surface, and are nearly circular in outline, but, apart from these differences, they show the same details of structure observed in *Entimus imperialis*. The patchy, inclined reflection, the hatching of fine lines in each of the differently colored reflecting areas, and the lamellar cleavage of the broken scales are even better defined. The increase in spacing of the surface striae with decrease in tilt of the reflection plane is very evident, and resembles the appearance of "pearlite" surfaced where its lamellae are inclined.

The whole set of optical properties, color distribution and alteration, and the behavior on penetration by liquids are the same as those of the preceding specimen.

Another scale-bearing beetle, representative of a widely studied species, is *Cyphus varnhageni* Germ. The structural and optical properties of its scales correspond closely to those of the two preceding specimens. The scales are oval, attached to the integument at one end, and their color is even more "patchy"; a mosaic of 10 or 15 colored areas may be seen on a single scale. The striae in these colored areas are well defined, but far from regular in many instances, and may have almost a *moiré* appearance. Correspondingly, the reflection is less perfectly specular.

Because the scales are divided into so many colors, and have such small reflecting areas, they do not appear as metallic to the naked eye as those of the specimens just described.

Eupholus azureus is even less metallic, and appears to have almost an "enamel" lustre; under the microscope small, closely adherent, deep blue scales are visible. On the under parts of the insect these shade into lighter greenish blue. Microscopically they are very similar to the scales of *Cyphus*, with numerous patches of color (violet to greenish-blue) on a single scale. The reflections are inclined and the striae are relatively irregular. The small size of the scales, and the number of reflecting patches on each gives a matte lustre to the specimen.

Another beetle, *Hoplia cerulea*, appears to constitute an exception to the general type of optical and structural properties shown by the scale-bearing beetles, in that there is no inclined reflection or mosaic distribution of coloring in the scales. These have slightly embossed or "pebbled" surfaces, which reflect specularly, and spread the light over an appreciable angle, so that to the naked eye they are only moderately metallic. The laminated fractures, behavior on penetration with liquids, and color changes with angle, pressure, or permeation are the same as shown by the scales of the other beetles.

Iridescence of Scales compared with that of Thin Films

The properties of the scales presented in the preceding pages need hardly be compared item by item with those of gratings or selectively reflecting substances to eliminate these from further consideration; their whole behavior is definitely at variance with either of these explanations. On the other hand, in spite of the efforts of the writer to avoid introducing the terminology of thin-film colors, the reader can scarcely have missed the rather striking resemblance between the behavior of the scales and that of thin color-producing films. That this resemblance is more than superficial is substantiated by detailed comparison of their optical properties.

1—The reflections are specular; a definite angle of incidence has a correspondingly definite angle of reflection. Microscopic "high-lights" on scales which are not perfectly plane demonstrate this plainly. Diffuse illumination does not cause the color to disappear.

2—The intensity of the reflection is high. This is true for a single thin film, as may be shown by means of a "model" prepared by picking up a colored film of varnish which has spread and hardened on the surface of water. Such films are highly metallic, with brilliant reflections. Multiple films, such as those of old Roman glass or iridescent $KClO_3$ crystals are even more perfect reflectors.[1]

3—The colors of the scales are readily recognized by comparison with artificial thin films, as corresponding to those of Newton's series, in the second or lower third orders.

4—The relationship to Newton's series is confirmed by the change in hue which takes place with increasing angle of incidence. In every instance, this is toward a color *lower in order*, and duplicates that of an artificial thin film held parallel to the reflecting plane of the scale.[2] The color change is marked, even with a rather small change of angle, and, to one who is familiar with the appearance of thin-film colors, is very characteristic.

5—The color produced on swelling the scale is predictable in all cases as that corresponding to an *increase in order* (thicker film). The swelled scales behave in all respects the same as the untreated ones.

6—The changes of color produced by compression of the scale are predictable in all cases as corresponding to a *decrease in order* (thinner film). This agreement is so perfect that the zones of altered color surrounding a compressed spot on a single scale are precisely similar to a portion of Newton's series. Moreover, the actual change in color may be witnessed under the microscope, and the gradual restoration of the color may also be followed. The destruction of color with extreme pressures corresponds to bringing the laminae into optical contact.

[1] These model thin films, single and multiple, are invaluable in the study of the optical properties of such systems. They are also useful in convincing people who, on the basis of their experience with soap-bubbles, doubt that such films are capable of exhibiting color and lustre equal to that of insects.

[2] This "decrease in order" of the color usually means a change toward violet (the color lowest in the second order) and some writers have tried to use this as evidence for selective reflection, but in a number of specimens the analogy breaks down completely. The change in hue is much greater than with any surface color known to the writer.

7—The distribution of colors on the scale or on the wing corresponds to slight variations of position in the series, (variation in thickness of film). Unless the coloring is in sharply defined patches the colors adjacent on the scale are those adjacent in the Newton's scale. The variation in hue may be very pronounced in the space of a few microns, in a manner more intricate than any possible pigment distribution.

8—The reflection and transmission colors are truly complementary in hue, if pigment is absent or neutral in color. This is true for all variations of angle, pressure, swelling, and distribution on the scale, so that the above paragraphs (3, 4, 5, 6, 7) describe both transmission and reflection colors.

9—In general the transmission colors are less saturated than the reflection colors, though for multiple films this difference is not so pronounced. (cf. the description of the flakes of decomposed glass, on page 324).

10—The polarization properties, where observable, are in full agreement with those of the reflections from thin color-producing films.[1]

11—The disappearance of iridescent color and metallic lustre when the scale is permeated by a liquid of its own index of refraction corresponds to that of thin films under similar conditions. The fact that liquids markedly higher or lower in refractive index do not cause complete loss of color is also consistent, particularly since the transmission color is diminished much more than is the reflection color.

12—The absence of any but neutral brown pigments, and of any diffraction phenomena likely to cause color is negative evidence of considerable significance.

The criteria enumerated above indicate the very close similarity between iridescent scales and thin film colors as regards their optical properties. Quantitative optical studies by Rayleigh and by Merritt also emphasize this resemblance. A single thin film is hardly an adequate postulate,[2] on account of the saturation of the transmission color, but multiple films are capable of exhibiting all the phenomena of the scale colors, and several writers[3] have come to the conclusion that they are the cause of the iridescent coloring.

In the opinion of the writer such a conclusion is justified on the basis of optical tests alone, but certain structural evidence is available which may have more weight with biologists, particularly since it throws light on the arrangement of the color-producing structure, and is wholly consistent with the optical phenomena exhibited. The essential structural features are as follows:

1—Lamellae, more or less parallel to the plane of the scale, are visible at fractured edges. Distorted sections may show lamellae separated.

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[1] Preston: "Theory of Light," 362 (1901).

[2] v. Lengerken (Biol der Tiere Deutschland, (Schulze) Lief. 12, Teil 40, p. 55) and Biedermann (*loc. cit.*) thought that "a thin layer of air between the two lamellae of the scale, functioning as a thin film" caused the color in most cases. They do not appear to recognize the possibility of multiple films or the inconsistency between the thickness of the interlamellar space and the colors produced.

[3] Süffert is the only one who bases his opinion on more than a few of the above points of likeness.

2—Penetration of viscous liquid through the color-producing structure is not instantaneous, but tends to proceed in layers, as if it were filling in the spaces between the lamellae.

3—Lamellae inclined to the plane of the scale are indicated by their successively projecting edges, which give the "beading" on the vanes of *Morpho* scales and the "finger-print" or "pearlite" pattern on the color patches of the beetle scales.

4—The dimensions of the color-producing structure are consistent with the type postulated, the lamellae of which would be only about 0.3-0.5 μ thick at most. There is space for a number of such films in any of the specimens examined.

The practical impossibility of any direct observation of the lamellar structure in sections perpendicular to its planes is to be expected from its dimensions, but it must be emphasized that the other evidence more than compensates for this deficiency.

As to whether the color-producing films are air between chitin, or chitin in air, or both, one cannot be certain, but since swelling agents (phenol vapor, etc.) alter the color in the direction corresponding to a thickening of the films, they may well be composed of chitin. If they were air, swelling the surrounding chitin should tend to thin them, unless some separating material swelled with the films and "opened" the air spaces.[1]

Assuming chitin films, the space between them need be very thin; an air film of thickness much less than that required to produce color would still serve to keep the chitin lamellae from being in optical contact, so that the distance between centers of the various planes might be little more than their thickness.[2]

The formation of such a systematic structure, remarkable as it is, puts no more strain on one's imagination than some of the other minutely intricate structures in insects; the lamellae are perhaps formed as a result of rhythmic precipitation in the scale, analogous to that involved in the synthesis of mother-of-pearl.[3]

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[1] Süffert puts a good deal of stress on the change in hue observed when the laminar structure is permeated by a liquid; he considers this as due to air films being replaced by films of liquid; of greater *effective* thickness because of higher refractive index. However, the scales are very susceptible to swelling by most liquids, and this would bring about the same sort of color change. This is evidenced by the fact that although the liquid may have been completely evaporated from the scale so that its full lustre and saturation of color is restored, the hue is frequently different from the original one, which is only regained after a moment's further exposure to the air.

[2] In all probability there is a small amount of structureless tissue irregularly distributed between the lamellae, since liquids do not spread perfectly evenly between them. This would help to maintain the films separate, and to restore them if they were pressed into perfect optical contact.

The air is so thin that india ink (carbon particles less than 0.2μ) is filtered, and only the aqueous vehicle penetrates between the lamellae.

[3] Ganguly: J. Chem. Soc., **1926**, 1381. Evaporation of gelatin and $Ca(HCO_3)_2$ solution yields an iridescent, laminated structure of $CaCO_3$.

Applications of the Thin-Film Theory to Type Specimens

The scales of the insects described above are alike as far as their important structural and optical properties are concerned, but there are certain points which need to be discussed more in detail because people have misinterpreted them in the past.

The *Uranidae* and other insects having scales of this type make no special demands on the theory; the multiple films may be in either lamina of the scale. Their plane is that of the scale, and in all respects their optical behavior is consistent with that of a system of multiple thin films, (say five to fifteen); the superposition of a vaned or meshed structure on the outer surface of the upper lamina modifies the visibility of the film colors, but does not prevent the recognition of their typical properties.

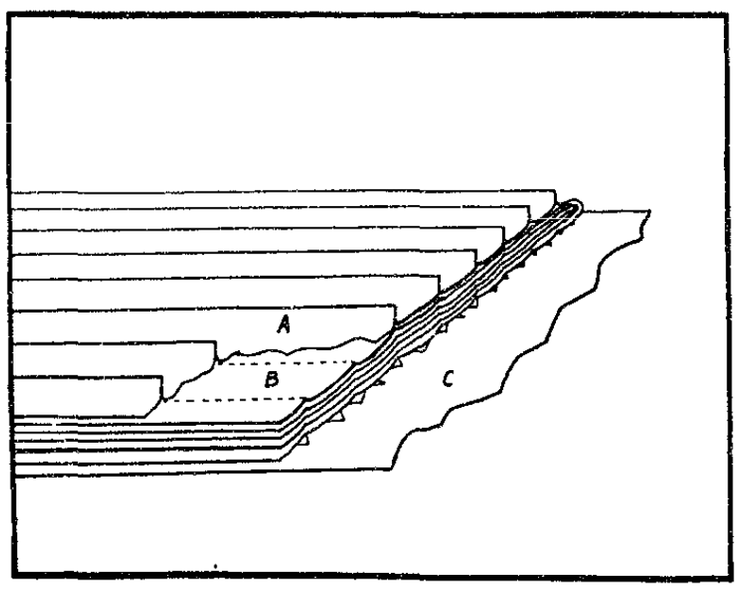


FIG. 1
Scale of *Urania* type (schematic).
A—thin vanes or ridges comprising longitudinal striations.
B—multiple films, the seat of the color.
C—lower lamella
Details of upper and lower surfaces may vary.

The pearly iridescent scales of *Argynnis* are of the same type as those of *Urania*, with no pigment, and less uniform films. The hues are recognizable as adjacent in the second order of Newton's series. The low intensity of the coloring may be due to only one or two films being present, or to the films not being alike in thickness, so that their colors tend to neutralize each other. The former explanation appears more probable from the appearance of the coloring.

The color-producing structure in the scales of *Ornithoptera poseidon* is essentially the same as that in *Urania*, but is enclosed within a dense "cuticle," and is less continuous in character, as indicated by the irregular loss and restoration of color with penetrating liquids. Also the reflecting surfaces are less perfectly plane, or are interrupted by intermediate tissue; the scattering of light and the finely stippled appearance of the scales by reflected light are

evidences of this. It may well be that the various lamellae are more or less "embossed" or that they are rather firmly supported by some sort of interpenetrating structure, or both these conditions may exist. This would account for the exceptionally great mechanical strength and rigidity of the scale, its lack of sensitiveness to pressure, and the moderate change with swelling agents.

In the case of the *Morphos* and other scales with inclined reflection localized in the vanes on their upper surface, the situation is rather more complex. As Süffert has demonstrated so convincingly, the lamellae must be inclined in

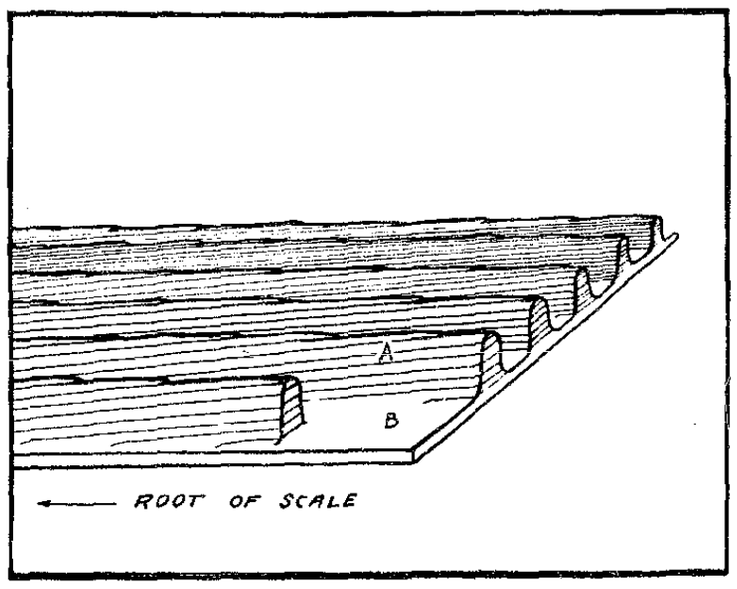


FIG. 2

Scale of *Morpho* type (schematic)
A—longitudinal vanes, consisting of inclined multiple thin films, the seat of the color.
B—basal layer.
Proximity of vanes and complexity of basal layer may vary.

the vanes and dip toward the root of the scale. The minuteness of the reflecting lamellae prevents a detailed study of their structure, but the oblique fracture which the vanes sometime show and the oblique extinction exhibited by them when flattened sidewise afford some confirmation of the optical tests. The closely spaced cross-markings or "beading" on the vanes of some of the scales are probably the edges of the successive lamellae, and one might even go so far as to estimate their thickness from the spacing.[1] The air space between the vanes is of no importance in the production of color, since isolated vanes act quite as well as those in systematic arrangement on the scale.[2]

Michelson's observations of anomalous phase differences in the light reflected by the scales of *Morhpo alga* are to be explained by the fact that he did not realize that the reflecting plane is inclined to the plane of the scale.

[1] Tilting, t, 10°-20°. Spacing of edges, s, 1-2μ; Spacing of laminae, $s \sin r$, 0.2 — 0.6μ.

[2] Onslow concluded that the vanes and the air layers between them acted as multiple films on edge. He apparently did not recognize that a single vane was capable of producing full color, or that the color may be seen with illumination strictly edgewise of the vanes. The vanes, seen flatwise, produce no color, though this position should give a maximum brilliancy according to Onslow's hypothesis.

He ignored completely the loss of color on penetration, yet concludes in favor of "surface color", not only for *Morpho* and *Papilio* but for all iridescent butterfly scales.

Entimus imperialis is typical of the scale-bearing beetles, which reflect light from a plane not parallel with that of the scale, and which frequently show several sharply defined, differently colored reflecting areas on a single scale. Here the lamellar structure fills the interior of the scale, and is enclosed by the cuticle. The lamellae are tilted in different directions in the different "patches" of color, and the "finger-print" or "pearlite" pattern in these is

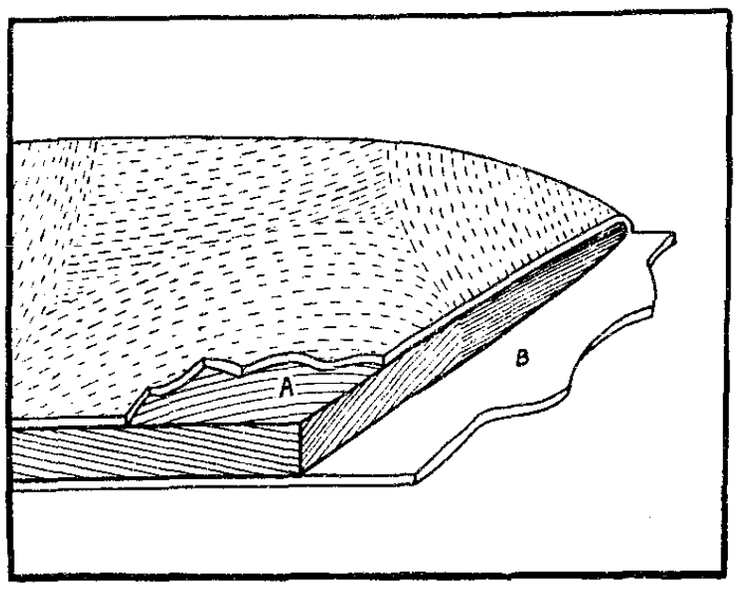


FIG. 3
Scale of *Entimus* type (schematic)
A—multiple thin films, the seat of the color.
B—"cuticle" enclosing lamellar structure.

from the edges of the successive thin films. The lines of this pattern closest together where the films are inclined most, and where they are farther apart the tilt of the reflecting surface is measurably less[1] (just as the grain of wood is varied by cutting more or less tangentially).

Biedermann and Mallock, who studied *Entimus* and *Cyphus* scales, considered their color to be due to thin films; Michelson admitted that the color could not be ascribed to selective reflection, on account of its destruction on penetration with liquids, but "the colours exhibited by these scales are so vivid and varied, and the changes so rapid with varying incidence that it was at once evident that the effect must be due to diffraction from regular striations" so he proceeded to calculate their interval and to postulate a "sawtooth" grating structure. He concluded that "the colour in this case is due to fine striations on the interior surface of the scale." Onslow doubted this on the basis of the brilliant transmission colors, the lack of sufficient regularity of the "striations," and the unimpaired coloring in diffuse light. He found

[1] Calculations of the spacing of the laminae (cf footnote 1, page 352) indicate a distance of probably less than 0.3μ between centers, which is in very fair agreement with the thickness of film corresponding to the colors exhibited by the scales.

evidence of inclined multiple films in some of the sections he studied, but in spite of all this he is apparently undecided between thin films and some sort of a "laminary grating" as the cause of the color. The second and third of Onslow's objections just cited apply quite as well to this postulate as to Michelson's "saw-tooth" grating.

Conclusion

The positive and negative evidence presented in the foregoing pages fits together well enough to justify still further the opinion which so many workers have had in the past—that the colors of iridescent scales are those of thin films. Any other assumption will not fit the facts, while this one fits them in a most consistent fashion. Because the details of the color production have not been discussed very definitely by most writers, and because only a relatively small part of the evidence was mustered by any one of them, the writer was particularly pleased to read Süffert's paper on butterfly scales, which reached him when the present work was being written up. The criteria utilized and the conclusions drawn are very closely concordant. The extended treatment of the optics of thin films, single and multiple, and the excellent color plates are especially to be commended to the attention of the reader, as supplementing the present article. The entire work constitutes a most convincing corroboration of the thin-film hypothesis.

Iridescent scales about which there is any question will probably fall rather definitely into one of the three classes described above, and the application of the various tests and lines of reasoning outlined should enable those interested to deal with such specimens.

The conclusions of this paper are as follows:

1—Iridescent wing membranes owe their color to multiple thin films separated by material of slightly different refractive index.

2—Iridescent scales are of three main types, each of which owes its color to multiple thin films separated by air.

3—In scales of the *Urania* type the color-producing lamellae are parallel to the plane of the scale, and may be overlaid by a ribbed or meshed structure.

4—In scales of the *Morpho* type the color-producing lamellae are in the vanes on the upper surface of the scale, and are inclined toward the root of the scale.

5—In scales of the *Entimus* type the lamellae are enclosed by a cuticle, and are tilted in different directions in sharply defined areas.

6—The fine striations common on insect scales are not related to the iridescence visible under ordinary conditions.

7—Selective reflection ("surface color") is not exhibited by iridescent insect scales.

Laboratory of Chemical Microscopy
Cornell University.

AQUEOUS SOLUTIONS OF SODIUM SILICATES. V.

OSMOTIC ACTIVITY, LOWERING OF VAPOUR-PRESSURES AND FREEZING-POINTS

BY R. W. HARMAN

Introduction

In the elucidation of the problem of the behaviour of solutions of silicates, the osmotic activity i. e. the nature of the ions and their concentrations, plays a very important part. The determination and discussion of the concentration and activity of sodium ions and of hydroxyl ions of aqueous solutions of sodium silicates of varying ratios and concentrations have already been communicated.[1] Heretofore, the silica in solution has always been thought to be colloidal, due, no doubt, to preconceived ideas arising from the colloidal nature of silicic acid, using the term silicic acid in a wide sense to cover all those forms of hydrated silica or hypothetical silicic acids, met with in the literature. From conductivity measurements[2] and from transport number experiments[3] evidence has been brought forward of the existence of silicate ions, and further work on diffusion through semi-permeable membranes to be communicated shortly leaves no doubt as to their existence.

The determination of the total concentration of the ions is perhaps the most important part of this investigation into the nature of aqueous solutions of sodium silicates. Having obtained a knowledge of the total crystalloidal content of these solutions, together with the hydroxyl and the sodium ion concentrations, the question of the relative amounts of colloidal and crystalloidal silica, with the possibility of ion adsorption, or of micelle formation, may be definitely discussed.

Of the many methods by which the osmotic activity of a solution may be measured, the lowering of the freezing point is, omitting exceptional cases, the best. The lowering of the vapour pressure is also capable of accurate measurement and has the advantage that it may be carried out at any temperature, thus obviating the necessity of correcting the osmotic pressure for temperature. Since a method of measuring the vapour pressure had recently been worked out in this laboratory and its application had met with success in an investigation on the activity of HCl solutions, it was decided to try this same method with silicate solutions; but the results as explained later, have not been altogether satisfactory. The freezing point method was then employed and the conclusions deduced herein are mainly from the results so obtained.

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[1] Aqueous Solutions of Sodium Silicates, III, IV. J. Phys. Chem., **30**, 917, 1100 (1926).
[2] Harman: J. Phys. Chem., **29**, 1155 (1925).
[3] Aqueous Solutions of Sodium Silicates, II. J. Phys. Chem., **30**, 359 (1926).

VAPOR PRESSURES

Experimental

The method was essentially the same as that used by Dobson and Masson[1] for measuring the vapour pressure of HCl solutions. It consists in saturating a measured current of gas, (nitrogen) with water vapour, by bubbling the nitrogen through the solution, and then absorbing and weighing this vapour. The vapour pressure follows from the gas laws when we know the volume occupied by the gas in the saturator.

The apparatus, made of hard glass, was a double apparatus, the first part consisting of saturators containing pure water followed by an absorber of H_2SO_4, the other part, of saturators containing the silicate solution followed by an absorber.

The great advantage of this type of double apparatus is that it may be operated in two ways:—

(1) to measure the actual vapour pressure of the water and of the solution, called the absolute method, A.

(2) to measure the vapour pressure of the silicate solution relatively to that of the water, relative method, R.

In the first way, the volume and pressure of nitrogen saturated with water vapour, and the weight of water vapour so required to saturate it, must be measured, whence can be calculated both the vapour pressure of the solution and of the pure water, the latter thus serving as a check on the accuracy of the experiment. Operating in this way, the passage of about 10-12 litres of nitrogen meant an increase in the absorbers of from 0.2-0.3 gram. However, the greater the amount of water vapour absorbed and weighed the greater the accuracy of the experiment. This was better achieved in the second method of operation, where the nitrogen was allowed to bubble through for about 24 hours, whereby the amount of water vapour absorbed was from 1 to 2 gm. In this method of operation the volume of nitrogen was not measured, so only the vapour pressure of the solution relatively to that of the water could be calculated.

The experiments were carried out at 25°C, the apparatue being immersed in a water thermostat electrically heated and regulated to 25° C ± 0.01.

The solutions used, their composition, concentration and preparation, the precautions taken, etc., were the same as those already quoted in the previous publications on this subject by the author.

Accuracy of Results

(1) *The absolute method, A.* The fact that the vapour pressure of water at 25° C can be calculated provides a most useful check and indication that the apparatus is working satisfactorily. One or two runs with each silicate solution experimented upon were usually made, but the values of the vapour pressure of water or of the silicate solution generally differed by as much as

[1] J. Chem. Soc., **125**, 668 (1924).

error is not surprising when we consider that the accuracy depends upon.—

(1) The amount of water vapour absorbed. This was about 0.2 gm., the total weight of the absorber and the H_2SO_4 being about 50 gm.

(2) The measurement of the excess pressure in the saturator. This fluctuated slightly over a run, but with a constant-level device attached to the aspirator the pressure could be measured to within 0.1 mm.

(3) The measurement of the volume of nitrogen collected. This volume was accurate to within 0.01%. By using great care and making several runs with the same solution it was possible to obtain the vapour pressure to within

TABLE I

Vapour Pressures

N_w	Method	Vap. Press. H_2O	Vap. Press. Soln.	Lowering in mms.	Mean Lowering	Calc. lowering	Expt. lowering / calc. lowering
			Ratio 1:1				
2.427	A	23.70	22.61	1.09			
	A	23.70	22.68	1.02	1.06	0.5096	2.08
	R	—	22.62	1.08			
1.062	A	23.70	23.20	0.50			
	A	23.70	23.12	0.58	0.55	0.2230	2.46
	R	—	23.12	0.58			
0.41	A	23.69	23.39	0.30			
	R	—	23.41	0.29	0.29	0.08610	3.36
0.102	A	23.71	23.63	0.08	0.08	0.02142	3.73
	R	—	23.62	0.08			
			Ratio 1:2				
2.0	A	23.70	23.24	0.46			
	R	—	23.25	0.45	0.45	0.42	1.08
	R	—	23.25	0.45			
1.0	A	23.69	23.39	0.30			
	R	—	23.38	0.30	0.31	0.21	1.49
0.5	A	23.70	23.51	0.19	0.20	0.105	1.90
	R	—	23.49	0.21			
0.2	R	—	23.60	0.10	0.10	0.042	2.38
	R	—	23.60	0.10			
0.1	R	—	23.65	0.05	0.055	0.021	2.61
	R	—	23.64	0.06			

0.01 mm. With the more concentrated solutions of ratio 1 : 1, where the lowering is in the neighbourhood of 1 mm., this 1% error is allowable, but with dilute solutions, e. g. one containing 0.2N crystalloidal matter, where the lowering is only 0.04 mm., the error in the vapour pressure lowering is 25%.

(2) *The relative method, R.* By allowing the nitrogen to pass through from 24 to 48 hours the weights of water vapour absorbed were increased to % gm. and the error due to their measurement practically eliminated. The error introduced by the measurement of the nitrogen has entirely disappeared, the calculation now being independent of the volume of nitrogen. Therefore the accuracy depends almost entirely upon the precision with which the excess pressure in the saturators can be measured, and this as stated previously could be determined to within 0.1 mm. of mercury. This method gave much more concordant readings, the accuracy being within 0.005 mm% of mercury, but even this means an error of 10% in the lowering of the vapour pressure of a dilute solution containing 0.2N crystalloidal matter. Hence the reason for making freezing point measurements as well.

Results

In Table I are given the results of vapor pressure measurements for ratios $Na_2O:SiO_2$, 1:1 and 1:2. Under the heading method is given the manner (absolute, A, or relative, R) in which the vapour pressure was found. Column 7 contains the calculated value of the lowering of the vapour pressure for the cited normality for an ideal non-associating, non-dissociating compound and column 8 the ratio of the experimentally found lowering to that of the calculated lowering, in other words, the van't Hoff factor "*i*".

These results will be discussed and compared with the freezing point results given below. However, the older method of calculating the molecular weight or degree of ionisation, involving the assumptions and conceptions upon which the van't Hoff factor "*i*" is based is probably not so accurate or in as close accordance with experimental facts as some of the more recent theories. Therefore an attempt will be made to interpret these results from the point of view of the activity theory.

Calculation of Activity Coefficients for Ratios 1:1 and 1:2 from Vapour Pressure of Solvent.

The method of calculating the activity coefficient of a solute for concentrated solutions from the vapour pressure of the solvent, given in Lewis and Randall's "Thermodynamics", has been strictly followed and the results are given in Table II, where the notation employed by Lewis and Randall has been followed. The first column gives the molality of Na_2SiO_3, the second gives p_1 the vapour pressure of water from the solution divided by p° the vapour pressure of pure water. The third column, under N_1/N_2 gives the mol ratio of the two constituents of the solution, i. e. the mol fraction of water divided by the mol fraction of the silicate. The values of N_1/N_2 have been calculated from the molality m by means of the conversion table.[1] If we plot

[1] Lewis and Randall: "Thermodynamics," Appendix 1, p. 609 (1923).

N_1/N_2 against 10 + log. $p_1/p_1°$, we get the difference between the two values of log A_2(A_2 being the activity of the solute) by obtaining the area under the curve. This quantity is proportional to A_2, and by taking the fourth root, i. e. assuming ν, the number of ions from complete dissociation of the solute molecule at infinite dilution, equal to 4, and dividing by m, we get a series of values, $k\gamma$, proportional to γ, the activity coefficient.

TABLE II

m	$p_1/p_1°$	N_1/N_2	10 + log $p_1/p_1°$	$k\gamma$
		Ratio 1:1		
1.213	0.955	41.76	9.9800	0.824
0.531	0.973	99.63	9.9881	1.364
0.200	0.988	298.0	9.9948	1.625
0.051	0.996	999.0	9.9983	1.930
		Ratio 1:2		
1.0	0.9811	27.4	9.9917	1.0
0.50	0.9872	57.0	9.9944	1.8734
0.25	0.9917	110	9.9964	3.3016
0.10	0.9959	510	9.9982	6.232
0.05	0.9977	999	9.9990	8.824

The values of $k\gamma$ in the last column of Table II give, of course, only comparative values of γ over the molalities quoted, because no measurements of vapour pressure are accurate enough in extremely dilute solution to warrant extrapolation to $\gamma = 1$. However, as will be seen later, when γ is calculated from freezing point measurements, the value of k can be found and hence γ from these vapour pressure calculations can be determined. This is done later on where γ from vapour pressure and from freezing point measurements are compared.

Freezing Point Measurements

Experimental

The ordinary laboratory or Beckmann method was used, as, at first, these freezing point measurements were intended only as a check on the vapour pressure measurements; but when it was discovered that the vapour pressure method was unsatisfactory, except for concentrated solutions, freezing point determinations of all the ratios viz., 2:1, 1:1, 1:2, 1:3, 1:4 were made at concentrations ranging from 0.005 N_w to 2.0 N_w. The usual precautions were taken; the temperature of the cooling bath, was maintained 2-3° C below the observed freezing point, and the amount of supercooling did not generally exceed 0.3°C. The temperatures were read correct to 0.002°C.

Results

Table III contains the results under the headings N_w or weight normality; m, molality, i. e. gm. mol. wt. ($Na_2O \times SiO_2$) per 1000 gms. solvent; Δ, observed lowering in degrees; Δ/m, molecular depression; "i" $= \frac{\Delta}{m \times 1.858}$, i. e.

TABLE III

Wt. Normality. N_w	Molality. m	Observed lowering Δ	Molecular Depression $\frac{\Delta}{m}$	Molec. depression / molal low. at inf. dil. for ideal sub. $i = \frac{\Delta}{m \times 1.858}$		
					Loomis	Kahlenberg and Lincoln
			Ratio 1:1			
2.435	1.217	4.290	3.525	1.89		
1.062	0.531	2.160	4.067	2.18	2.1	
0.204	0.102	0.548	5.370	2.88	2.8	2.9
0.100	0.050	0.291	5.820	3.13	3.1	3.4
0.05	0.025	0.155	6.600	3.55	3.4	3.7
0.02	0.010	0.070	7.00	3.75	3.5	3.7
0.01	0.005	0.036	7.20	3.87		
			Ratio 2:1			
0.796	0.398	2.225	5.59	3.0		
0.398	0.199	1.195	5.97	3.2		
0.159	0.079	0.495	6.26	3.35		
0.0796	0.0398	0.3002	7.54	4.0		
0.0398	0.0199	0.170	8.45	4.5		
0.0159	0.0079	0.080	10.12	5.4		
			Ratio 1:2			
2.450	1.225	2.140	1.747	0.94		
1.100	0.550	1.215	2.209	1.94		
0.500	0.250	0.770	3.080	1.65		
0.204	0.102	0.415	4.068	2.19		
0.100	0.050	0.255	5.100	2.74		
0.050	0.025	0.140	5.600	3.01		
0.020	0.010	0.060	6.000	3.22		
0.010	0.005	0.033	6.600	3.55		
			Ratio 1:3			
2.00	1.00	1.465	1.465	0.772		
1.00	0.50	0.985	1.970	1.06		
0.50	0.25	0.680	2.720	1.46		
0.20	0.1	0.405	4.050	2.17		
0.10	0.05	0.220	4.400	2.36		
0.05	0.025	0.130	5.200	2.73		
0.02	0.01	0.055	5.500	2.96		
0.01	0.005	0.030	6.000	3.22		
			Ratio 1:4			
2.00	1.00	1.050	1.050	0.565		
1.00	0.50	0.795	1.590	0.855		
0.50	0.25	0.540	2.160	1.16		
0.20	0.10	0.340	3.400	1.83		
0.10	0.05	0.215	4.300	2.31		
0.05	0.025	0.125	5.000	2.69		
0.02	0.01	0.055	5.500	2.96		
0.01	0.005	0.028	5.600	3.01		

the ratio of the observed molecular depression Δ/m, to the molal lowering at infinite dilution, 1.858, of an ideal substance, (the van't Hoff factor "i"). The values of "i" calculated from the results of Loomis, and of Kahlenberg and Lincoln for Na_2SiO_3 are given for comparison.

Table IV shows the molecular depressions, Δ/m, at round concentrations collected together for comparison.

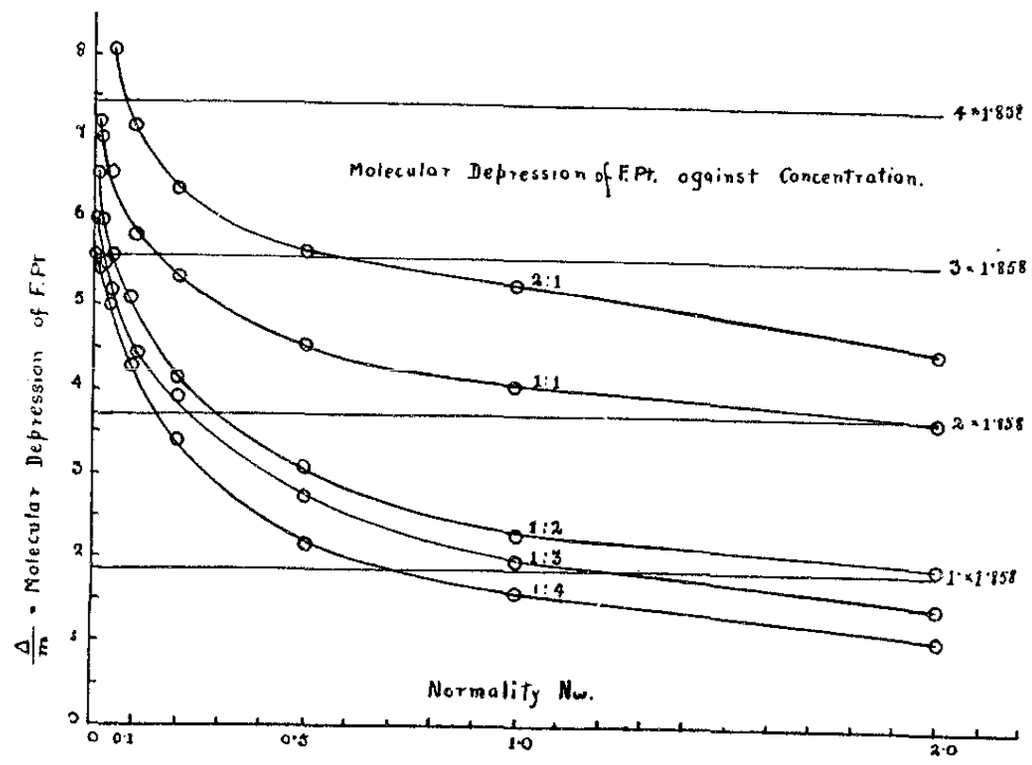


FIG. 1

The graphs in Fig. 1 show the molecular depression Δ/m plotted against the molality. The horizontal lines indicate the several values of the van't Hoff factor "i".

TABLE IV

N_w	m	Molecular Depression, Δ/m				
		2:1	1:1	1:2	1:3	1:3.95
2.00	1.00	4.274	3.675	1.925	1.465	1.050
1.00	0.50	5.295	4.075	2.265	1.970	1.590
0.50	0.25	5.667	4.550	3.105	2.720	2.160
0.20	0.10	6.410	5.370	4.068	4.050	3.400
0.10	0.05	7.155	5.820	5.100	4.400	4.300
0.05	0.025	8.083	6.600	5.600	5.200	5.000
0.02	0.01	9.385	7.000	6.000	5.500	5.500
0.01	0.005	10.41	7.200	6.600	6.000	5.600

Table V shows the values of $\frac{\Delta}{m \times 1.858}$ i. e. the van't Hoff factor "i" for all the ratios at round concentrations collected for comparison.

TABLE V

N_w	m	Van't Hoff factor "i" $= \frac{\Delta}{m \times 1.858}$				
		2 : 1	1 : 1	1 : 2	1 : 3	1 : 4
2.00	1.00	2.30	1.98	1.03	0.772	0.565
1.00	0.50	2.85	2.19	1.22	1.06	0.855
0.50	0.25	3.05	2.45	1.67	1.46	1.06
0.20	0.10	3.45	2.88	2.19	2.17	1.83
0.10	0.05	3.85	3.13	2.74	2.36	2.31
0.05	0.025	4.35	3.55	3.01	2.73	2.69
0.02	0.01	5.05	3.75	3.22	2.96	2.96
0.01	0.005	5.60	3.87	3.55	3.22	3.01

Comparison of Vapour Pressure and Freezing Point Results

Before discussing the freezing-point results it is interesting to compare them with those obtained from vapour-pressure measurements.

In Table VI are given the values of "i" obtained from v.p. and F.Pt. measurements for ratios 1:1 and 1:2.

TABLE VI

Weight normality N_w	Molecular depression molal depr. at infin. dil. of ideal subs.	
	Vapour pressures	Freezing points
	Ratio 1:1	
2.427	2.08	1.89
1.062	2.46	2.18
0.41	3.36	2.60
0.102	3.73	3.13
	Ratio 1:2	
2.00	1.08	1.03
1.00	1.49	1.22
0.50	1.90	1.67
0.20	2.38	2.19
0.10	2.61	2.74

For ratio 1:1 the values from vapour pressure are considerably higher; this is partly accounted for by the difference in temperature (25°) as these results have not been corrected for temperature in the comparison. In ratio 1:2 there is much better agreement. This is probably due to hydrolysis being greater in 1:1 than 1:2, hence the 25° difference in temperature will have more effect in 1:1 than in 1:2.

The agreement between the two methods is on the whole quite satisfactory; this is shown graphically in Fig. 2 where the molecular depression is plotted against the concentration. This graph shows Δ/m from vapour pressure and F.Pt. measurements and also Loomis' results from F.Pt.

Presentation of Results according to the Activity Theory

The accuracy of the freezing point results does not really warrant the calculation of activity coefficients therefrom as Lewis has based his calculation upon the very accurate work in dilute solution made possible by the recent development in freezing point technique due to the work of Hausrath, Bedford, Adams, Richards etc. However, useful information will be gained, but it must be borne in mind that the values for the activity coefficients given below are not claimed to be strictly correct on this account.

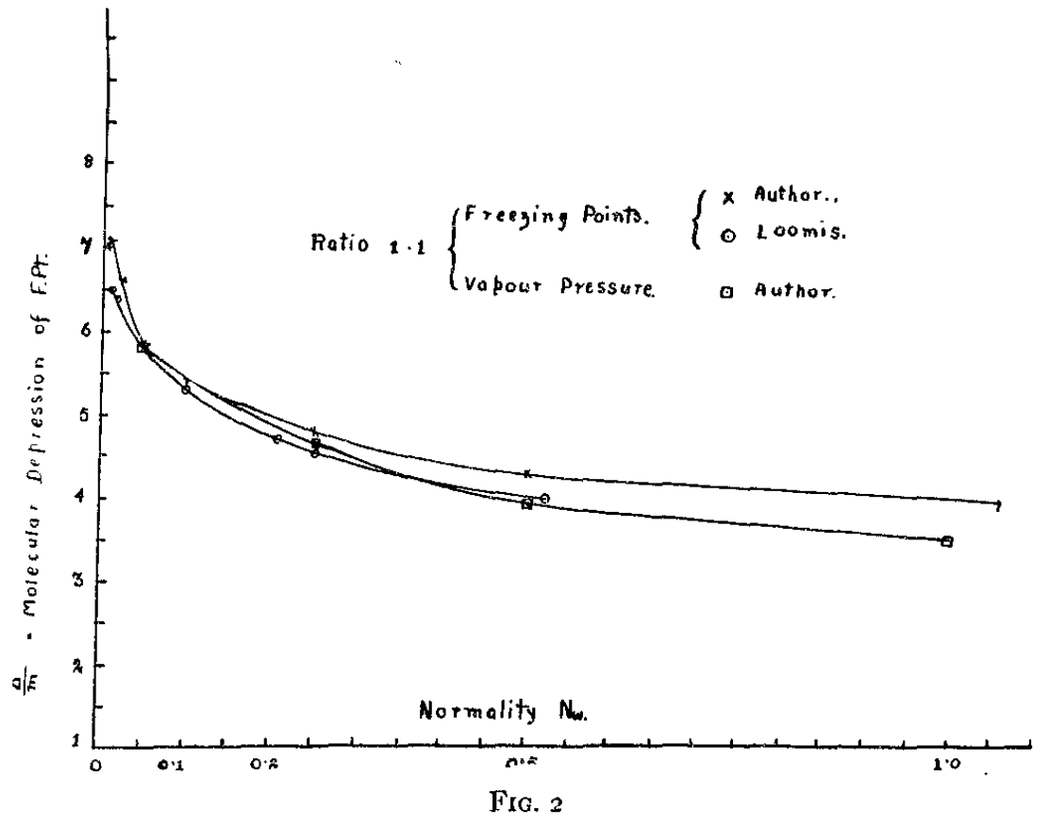


FIG. 2

Calculation of Activity Coefficients at 25°C from Freezing Points

The method of calculation given in Lewis and Randall's "Thermodynamics" has been followed.

The question of assigning a value to ν in the equation[1] $j = 1 - \frac{\Delta}{\nu \lambda m}$ for $Na_2O.xS_1O_2$ where x is 1, 2, 3, 4 etc. respectively, is a very difficult one. If ν be put equal to three for ratios 1:1, 1:2 and 1:3 quite impossible and absurd values are obtained. In view of the results already obtained for $\frac{\Delta}{m \times 1.858}$, it seems most rational, and cannot be very incorrect, to put ν equal to 4 for 1:1, 1:2, and 1:3 ratios. In order to get comparable values on the same basis ν has been put equal to 4 for the other ratios as well.

[1] Lewis and Randall: "Thermodynamics," Equation 2, p. 342 (1923).

In the following calculations use has been made of the Lewis-Linhart relationship $j = \alpha\ \beta m$ to determine $\int_0^m -j\ d(\log m)$ up to m = 0.01, by means of the equation $\int_0^{0.01} -j\ d(\log\ m) = \frac{-\beta}{2.303\alpha} \cdot (0.01)\,\alpha$ while for values of m greater than 0.01 the graphical method has been followed for the evaluation of

$$\int_m^0 -j\ d(\log m).$$

The calculation of γ for ratio 1:1 follows in Table VII.

TABLE VII

Calculation of γ for Na_2O:SiO_2, 1:1, from F.Pts. (assuming $\nu = 4$ ions)

N_w	m	Δ	$j = 1 - \frac{\Delta}{\nu\lambda m}$	log j	$\frac{j}{2.303}$
2.435	1.217	4.290	0.5145	$\bar{1}.7114$	0.2234
1.063	0.531	2.160	0.3108	$\bar{1}.4925$	0.1349
0.204	0.102	0.548	0.2770	$\bar{1}.4425$	0.1203
0.101	0.050	0.291	0.2170	$\bar{1}.3365$	0.0942
0.050	0.025	0.165	0.1118	$\bar{1}.0483$	0.0485
0.020	0.010	0.070	0.0580	$\bar{2}.7634$	0.0251
0.010	0.005	0.036	0.0313	$\bar{2}.4955$	0.0136

From the plot of log j against log m, $\alpha = 0.086$, $\beta = 3.0$, whence, by means of the equation $\int_0^{0.01} -j\ d(\log m) = \frac{-\beta}{2.303\alpha}(0.01)^{\alpha}$, values of $\int_0^m -j\ d(\log m)$ for concentrations 0.005 and 0.01 have been obtained.

m	$\frac{j}{2.303}$	$\int_0^m j\ d(\log m)$	$-\log \gamma$	γ
0.005	0.0136	0.0218	0.0354	0.9217
0.010	0.0251	0.0263	0.0514	0.8884
0.025	0.0485	0.0602	0.1087	0.7785
0.050	0.0942	0.1095	0.2037	0.6256
0.102	0.1203	0.1836	0.3039	0.4967
0.531	0.1349	0.4243	0.5582	0.2766
1.217	0.2234	0.5893	0.8127	0.1539

TABLE VIII

Activity Coefficient, γ, from F. Pt. Based on $\nu = 4$, i. e. each molecule gives 4 ions at infinite dilution

m	NaOH	1:1	1:2	1:3	1:4
0.005	0.950	0.922	0.731	0.604	0.412
0.001	0.920	0.888	0.599	0.484	0.342
0.025	0.867	0.778	0.456	0.359	0.244
0.050	0.820	0.626	0.358	0.252	0.171
0.100	0.765	0.497	0.259	0.179	0.109
0.500	0.700	0.280	0.080	0.052	0.029
1.000	0.680	0.192	0.035	0.029	0.015

The values of γ for NaOH above are taken from Harned.[1]

These results are plotted in Fig. 3.

[1] J. Am. Chem. Soc., **47**, 682 (1925).

Having calculated γ from freezing-points we can now find γ from vapour pressure measurements, where the quantity obtained was $k\gamma$, not γ.

The comparison is shown in Table IX.

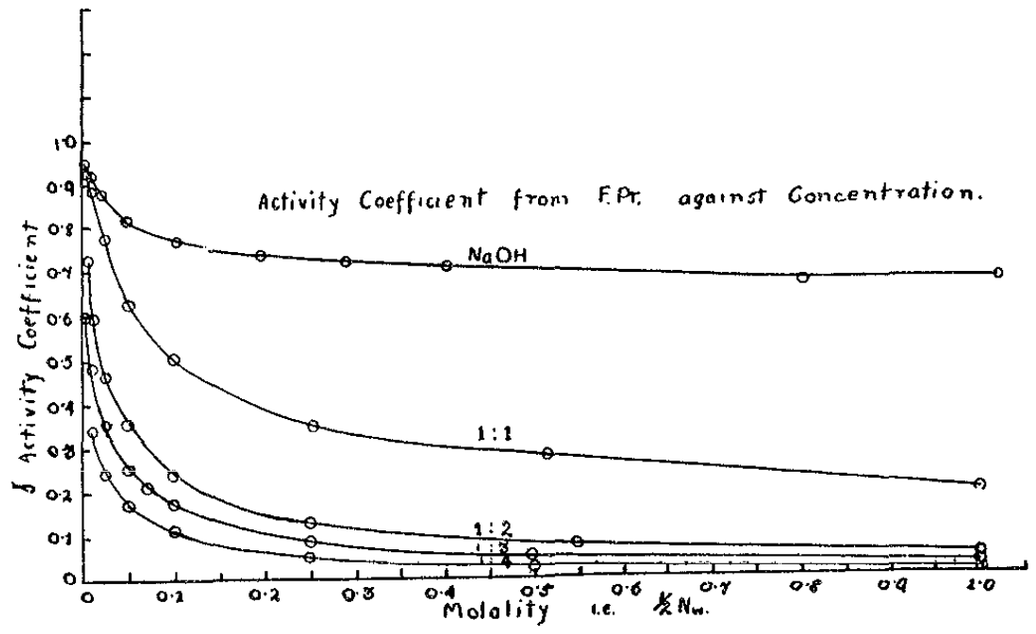


FIG. 3

TABLE IX

Comparison of Activity Coefficients calculated from V.P.'s and F.Pt's.

m	γ from V.P.'s	γ From F.Pt's.
	Ratio 1:1	
1.219	0.154	0.154
0.531	0.255	0.277
0.200	0.3035	0.329
0.051	0.3555	0.626
	Ratio 1:2	
0.10	0.035	0.035
0.50	0.066	0.080
0.25	0.116	0.130
0.10	0.219	0.539
0.05	0.309	0.358

Except in dilute solution (0.05 = m, ratio 1:1) where the percentage error in the vapour pressure measurement is large, the agreement is fair.

Discussion of Results

Such a problem, as this, namely of the behaviour and nature of substances in solution, can only be satisfactorily solved when our ideas regarding solutions in general are stabilised. At present the problem of solutions of electrolytes, and more particularly the anomaly of strong electrolytes, is being attacked along two main lines, both having thermodynamic considerations as their basis.

(1) In the first the idea of actual concentration of ions and undissociated molecules is regarded as the fundamental factor in determining the equilibrium between the different species. The conductivity method is regarded as reasonably accurate in determining such concentrations, but since the law of mass action, expressed in such concentration terms is known not to apply, modifications of this expressed by means of empirical coefficients e. g. Storch's equation have been applied with reasonable success.

(2) In the second mode of treatment, the conductivity method is discarded, and instead of the older conception of actual concentration of ions and molecules, a newer treatment correlating various thermodynamic relationships involving the effect of concentration or activity has been applied also with considerable success.

Considering the first method above, there are three assumptions which may be employed for the calculation of the degrees of ionisation,—

(1) The degree of ionisation is correctly given by the conductivity-viscosity ratio.

(2) van't Hoff's law is obeyed by the ions.

(3) van't Hoff's law is obeyed by the undissociated molecules.

Experimental data show that in general only one of these three assumptions can be true in the case of strong electrolytes, the acceptance of any one involves the rejection of the other two.

It has been pointed out by Bates[1] that the mistake is often made of calculating the degree of ionisation from freezing-point data by using the empirical expression of van't Hoff, $P = iRTC$, which implies that assumptions (1) and (2) above are simultaneously true.

However, until such time as the problem of solutions in general is elucidated, we can still derive much valuable information by making use of the earlier ionic theory and its underlying assumptions relating to ideal solutions. This line will be followed now, although the results from the activity standpoint will also be discussed.

Discussion of Results as calculated from the View-Point of the Activity Theory

Necessarily the whole series of results, based as they are on the one set of experimental data, are relatively the same as those observed when the freezing-point measurements are expressed in terms of the ideal ionic theory, but, as is to be expected from the nature of the two theories, the values of γ, the activity coefficient, are lower than the value of α, the degree of ionisation, calculated from conductivity or from the van't Hoff factor "i".

In considering the above values of γ in Table VIII, it must be borne in mind that they have been calculated, for all the ratios, (not for NaOH where $\nu = 2$) on the assumption that $\nu = 4$, i. e. that the solute molecule gives rise to 4 ions on complete dissociation at infinite dilution.

[1] J. Am. Chem. Soc., **37**, 1421 (1915).

The ratio 1:2 is thus very largely dissociated in dilute solution, but very little in concentrated solution; the almost equal values of γ in dilute solution, and the great difference in values of γ in concentrated solution, for Na_2SiO_3 and NaOH being noticeable from figure 3.

In ratio 1:4 the percentage dissociation has fallen considerably over the whole range of concentrations.

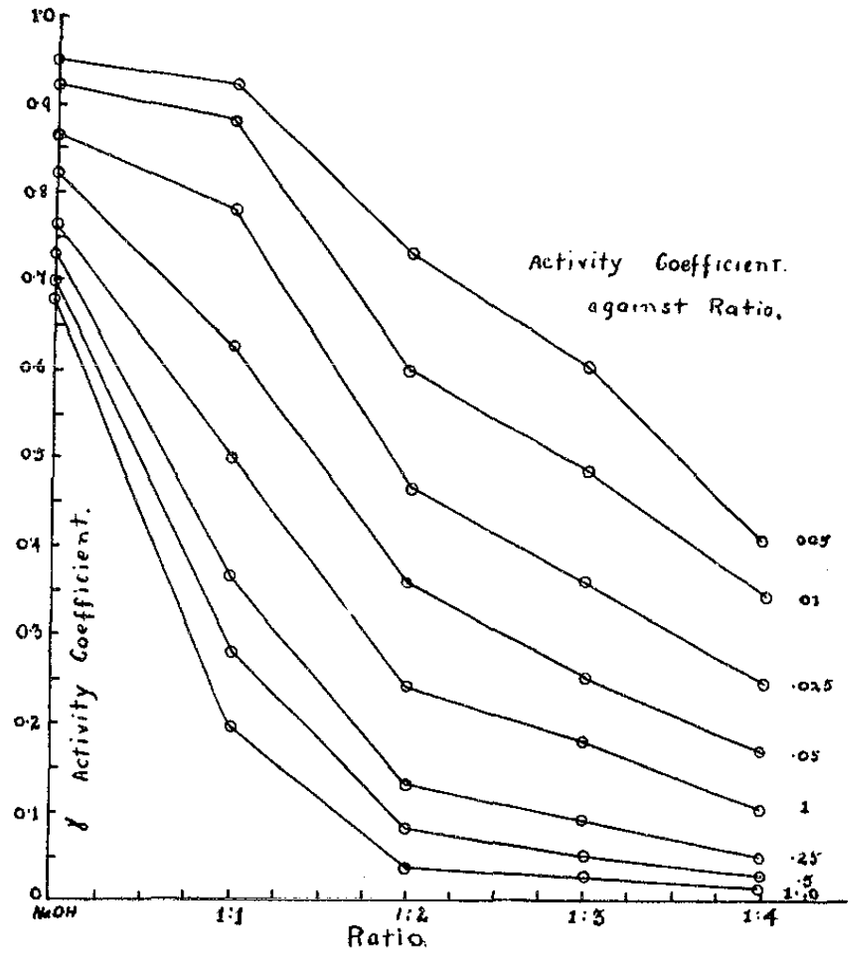


FIG. 4

In Fig. 4, γ is plotted against the ratio. As with all the other quantities measured and plotted in this series of investigations of aqueous solutions of sodium silicates, there are changes of direction in the curves at 1:1 and 1:2 for concentrated solutions, and at 1:2 for dilute solutions. At all concentrations the decrease in γ with increasing amounts of SiO_2 is practically linear after ratio 1:2.

The Results as calculated from the Earlier Ionic Theory

Considering Table V, we see that the greater the proportion of Na_2O in the ratio, the greater the value of "*i*", i. e. the crystalloidal content of the solutions decreases with increase of silica. This is brought out in the graphs in Fig. 5 where the molecular depression is plotted against the ratio. As was the case when conductivity, hydroxyl ion concentration and sodium ion concentration were plotted against the ratio, changes of direction in the curves

are again noted at ratios 1:1 and 1:2; at 1:1 in dilute solution and at 1:2 in the more concentrated solutions; while beyond 1:2, Δ/m falls regularly and linearly as the proportion of silica in the ratio increases.

Ratio 1:1

Ratio 1:1 is the definite crystalline salt, sodium metasilicate, Na_2SiO_3. The value of "*i*" indicates a fairly large degree of hydrolysis or ionisation, even in concentrated solution. In the most dilute solution investigated, 0.01 N_w,

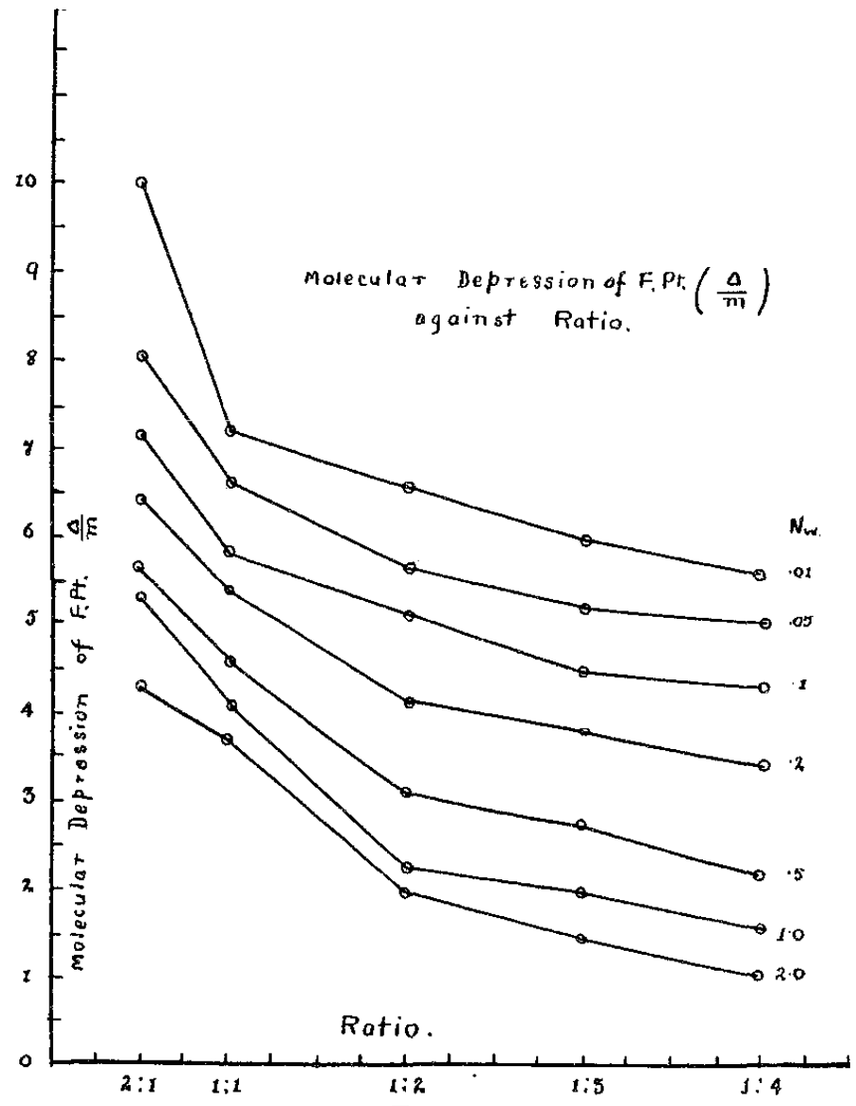


FIG. 5

the value 3.87 lies between 3, expected if total ionic dissociation took place, and 4, the consequence of total hydrolytic dissociation and total ionisation of the NaOH so formed, assuming in the latter case all the silica to be colloidal and to have no disturbing effect on the other constituents of the solution. If the latter view is correct, and assuming the laws of ideal solution to apply, then $\frac{3.87}{4} \times 100 = 97\%$ hydrolysis takes place, a value in very close agreement with the figure calculated from conductivity measurements[1] and with the

[1] Harman: J. Phys. Chem., **29**, 1155 (1925).

figure assigned by Kohlrausch[1] from conductivity measurements and also by Loomis[2] from freezing point measurements. However, only 27.8% hydrolysis is found by E. M. F. measurements (Part IV) a value confirmed by Bogue's E. M. F. measurements.[3]

Thus we have found 27.8% hydrolysis by E. M. F. measurements and 97% hydrolysis from freezing point lowering and from conductivity, assuming in the latter case the laws of ideal solution to hold, which at this concentration, 0.005 m, will not introduce a very serious error, and also assuming all the silica in solution to be colloidal. These two results are quite incompatible, but the assumptions with regard to the laws of ideal solution can in no way cause such a large discrepancy. Of the two values, the 27.8% found by E. M. F. measurements will be the more correct one.

Therefore we can state with certainty that, neither

(1) 27.8% hydrolytic dissociation into $2Na^{\cdot} + 2OH' +$ colloid H_2SiO_3 alone occurs, as this does not agree with the freezing-point results,

nor (2) is the silica or silicic acid formed, wholly, if at all, colloidal, i. e. SiO_3 ions must exist in the solution, and both hydrolytic and ionic dissociation must take place.

The interaction of sodium metasilicate and water may be represented as follows at very low concentration, where if hydrolysis has taken place in two stages the concentration of $HSiO'_3$ will be negligible:—

$$\begin{array}{ccccc} Na_2SiO_3 & \leftrightarrows & 2Na^{\cdot} & + & SiO_3'' \\ + & & + & & \\ 2HOH & \leftrightarrows & 2OH' & + & 2H^{\cdot} \\ & & \Updownarrow & & \Updownarrow \\ & & 2NaOH & & H_2SiO_3 \end{array}$$

From E. M. F. measurements there is 27.8% hydrolytic dissociation at concentration 0.005m (or $N_w = 0.01$). From sodium ion measurements there is 97.5% of the primary reaction

$$Na_2SiO_3 \leftrightarrows 2Na^{\cdot} + SiO''$$

at this concentration. The H_2SiO_3 formed, as indicated above, may be taken as all crystalloidal, which seems justifiable at this low concentration, and be capable of dissociating into H and SiO_3 ions, a reasonable possibility, in spite of the general belief to the contrary, and one which receives so much support from experimental evidence based upon conductivity measurements,transport number experiments, diffusion experiments, apart from the favourable evidence adduced herein, that it appears almost a certainty. Calculating the van't Hoff factor "i" upon this basis and making use of the OH and Na ion concentration, we get "i" = 3.52, whereas "i" from F. Pts. is equal to 3.87.

This is fairly good agreement, considering that it depends on ordinary laboratory freezing point technique, and on two independent sets of E. M. F.

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[1] Z. physik. Chem., **12**, 773 (1893).
[2] Wied. Ann., **60**, 531 (1897).
[3] J. Am. Chem. Soc., **42**, 2575 (1920).

measurements, and it not only supports the view that both hydrolytic and ionic dissociation take place but that a fairly correct percentage value has been obtained for both these dissociations.

Let us consider almost complete hydrolysis into NaOH and colloidal H_2SiO_3, according to the theory put forward by Kohlrausch[1] and by Loomis,[2] the extent of such hydrolysis, to be determined by the concentration of sodium ions,[3] but assuming the OH ions to be adsorbed to a large extent by the colloidal silica so that the actual OH ion concentration agrees with the percentage hydrolysis found by E. M. F. measurements. On this basis, for concentration N_w = 0.01, i. e. 0.005 m, "*i*" = 2.53, whereas from F. Pt. measurements "*i*" is 3.87. This non-agreement, clearly outside the bounds of experimental error, appears to afford definite proof against OH ion adsorption.

Ratio 1:2

Here there are three possibilities:—

(1) definite salt $NaHSiO_3$
(2) definite salt $Na_2Si_2O_5$
(3) aggregates or micelles.

(1) *definite salt* $NaHSiO_3$.

$$\begin{array}{ccccc} NaHSiO_3 & \leftrightarrows & Na^{\cdot} & + & HSiO_3' \\ + & & + & & + \\ HOH & \leftrightarrows & OH' & + & H^{\cdot} \\ & & \Updownarrow & & \Updownarrow \\ & & NaOH & & H_2SiO_3 \end{array}$$

Following the same reasoning as already given for ratio 1:1, and taking the values found for OH ion and Na ion concentrations, communicated in two previous papers, as giving the percentage hydrolytic and percentage ionic dissociation respectively, we get at concentration m = 0.05, since percentage hydrolysis equals 0.051 and percentage ionisation equals 0.60, "*i*" = 3.34, taking into account that the concentrations expressed herein are in terms of $Na_2O.2SiO_2$.

(2) *definite salt* Na_2SiO_5.

$$\begin{array}{ccccc} Na_2Si_2O_5 & \leftrightarrows & 2Na^{\cdot} & + & Si_2O_5'' \\ + & & + & & + \\ 2HOH & \leftrightarrows & 2OH' & + & H^{\cdot} \\ & & \Updownarrow & & \Updownarrow \\ & & 2NaOH & & H_2Si_2O_5 \end{array}$$

For the same concentration, 0.005 m, where percentage hydrolysis equals 0.051 and percentage ionisation equals 0.60, "*i*" = 2.5.

Since "*i*" from F. Pt. equals 3.50, on this evidence alone one would say that it is extremely probable that the salt $NaHSiO_3$ exists in solution.

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[1] Z. physik. Chem., **12**, 773 (1893).
[2] Wied. Ann., **60**, 531 (1897).
[3] Harman: J. Phys. Chem., **30**, 922 (1926).

(3) *aggregates or micelles.*

Several suggestions could be put forward to explain the values of "*i*" obtained but as all of these would be largely hypothetical, it seems better to defe- this for the moment, except to state that from transport number experiments we know that one proportion of SiO_2 carries one charge of electricity and so the ion is not the simple ion SiO_3, and from freezing point measurements the existence of the salt $NaHSiO_3$ seems most probable.

Thus for ratio 1:2 the existence of the acid metasilicate $NaHSiO_3$ agrees very well with all the experimental data so far given.

Ratios 1:3 and 1:4

When we consider ratios 1:3 and 1:4 and bear in mind the result of transport-number experiments at moderate concentrations, where it was found probable that there were three and four proportions of SiO_2 respectively per divalent charge we admit two possibilities:—

(1) definite salts,

$$Na_2O.3SiO_2aq.$$
$$Na_2O.4SiO_2aq.$$

ionising to give sodium and silicate ions of composition ($_3SiO_2aq$) and ($_4SiO_2aq.$)

(2) Aggregates or micelles of the composition $[m{\cdot}SiO_3{\cdot}n{\cdot}SiO_2aq.]^{m--}$ where (m+n)/m equals the ratio, or an aggregate containing amongst other constituents a number of SiO_2 equivalents approximately equal to the ratio per divalent charge.

Let us consider these two possibilities.

(1) *Definite salts.*

Calculating "*i*" as before for concentration m = 0.05, since hydrolysis is practically negligible and the percentage ionisations as given by Na ion concentration are 0.70 and 0.55 respectively for ratios 1:3 and 1:4 we get

ratio	"*i*" calculated	"*i*" from F. Pts.
1:3	2.40	3.22
1:4	2.10	3.00

Hence the existence of definite salts so ionising seems very unlikely.

(2) *Aggregate or micelle formation.*

In very concentrated solution the silicate probably exists as a very complex aggregate, which not only breaks up on dilution but also gives rise to $Na^{\cdot}$ and SiO_3'' or other simple silicate ions, these latter coalescing to form ionic micelles. Only on some such theory can the results from conductivity, transport numbers, hydroxyl and sodium ion concentrations, and freezing points be explained.

In solutions of these higher ratios the OH ion concentration is practically negligible, especially in concentrated solutions, and the sodium ion concentration as found by E. M. F. measurements accounts for only a small fraction of the total crystalloidal content as calculated from the lowering of the freezing point.

For example, at concentration $N_w = 0.01$, the normality due to Na ions is 0.011, while the total normality as found from freezing-points is 0.03, thus leaving 0.019 N to be accounted for either by the silica present, or by some form of undissociated silicate, or both.

In more concentrated solutions, e. g. 0.1 N_w, 1:4 ratio, where the total normality is found to be 0.23, the normality due to the Na ions is only 0.05.

It is not proposed to go into this question in this paper, but it is hoped to give a rational complete theory shortly when all the experimental data obtained have been published. It will be sufficient to indicate here that at present it appears that the ratios higher than 1:2 are not definite salts giving definitely determinable silicate ions in solution. Rather, having regard to the fact that the value for "*i*" is abnormally low in concentrated solutions and exceptionally high in dilute solutions, and to the results of transport number experiments, ionic micelles of the composition $(m.SiO_3.n.SiO_2aq.)^{m--}$ appear to be present, where m + n/m equals the ratio; and the following equilibria exist,—

(1) $SiO_3'' + [\text{colloid } SiO_2 \text{ aq.}] \leftrightarrows [m.SiO_3.n.SiO_2 \text{ aq.}]^{m--}$

and

(2) $[\text{Colloid } SiO_2aq.] \leftrightarrows \text{crystalloidal } H_2SiO_3 \leftrightarrows 2H^{\cdot} + SiO_3.''$

Evidence for equation (1) is also obtained from transport number experiments, while in a later paper it will be shown that equation (2) is not only true but takes place to a much greater extent than commonly supposed even in moderately concentrated solutions.

Until further work is done with the specific purpose in view of determining the exact constitution of the silicate in these high ratios i. e. of proving conclusively that it is or is not the SiO_3 ion which is here formed in dilute solution, and until more exact knowledge is gained concerning H_2SiO_3 itself, we can only state that micelle formation offers the best explanation of the experimental data given herein,

It must be emphasized that the foregoing suggestions of the existence of aggregates and ionic micelle are only tentative.

Summary

(1) Measurements of the lowering of vapour-pressure have been made by a dynamic method, for ratios $Na_2O : SiO_2$, 1:1 and 1:2 over a concentration range 0.1 — 2.5N_w, and the results expressed in terms of the earlier ionic theory and also in terms of the more recent activity theory.

(2) Lowering of freezing-points by the Beckmann laboratory method have been found for ratios 2:1, 1:1, 1:2, 1:3 and 1:4 over a concentration range 0.01—2.0N_w, and the results expressed in terms of the van't Hoff factor "*i*" and in terms of the activity theory.

(3) The results from V. P. and from F. Pts. are in fair agreement.

(4) Ratios 2:1 and 1:1, and to less degree 1:2, exhibit a high degree of osmotic activity, more especially in dilute solution. Ratios 1:3 and 1:4 show an abnormally low osmotic activity in concentrated solution but unexpectedly high in dilute solution.

(5) From the results it appears that ratio 1:1 is the salt Na_2SiO_3 undergoing both hydrolytic and ionic dissociation giving rise to $Na^{\cdot}$, OH' and SiO_3'' ions and H_2SiO_3, most of the latter being crystalloidal. Na_2SiO_3 is practically completely dissociated in dilute solution but only 27.8% hydrolytically. Ratio 1:2 is the definite salt $NaHSiO_3$, behaving like Na_2SiO_3 and giving rise to $Na^{\cdot}$, OH' and $HSiO_3'$ ions and H_2SiO_3. There is 0.60% dissociation at concentration 0.005 m but only 0.05% hydrolytic dissociation. The results from ratios 1:3 and 1:4 are not in accord with the view that these ratios are definite salts but agree well with the existence of complex aggregates in concentrated solution and of ionic micelle of the composition $[m.\ SiO_3.n\ .SiO_2aq.]^{m-}$ where $m + n/m$ = ratio; the following equilibria also existing

$$SiO_3'' + [\text{colloid } SiO_2\ aq.] \leftrightarrows [mS;O_3.n\ SiO_2\ aq.]^{m--}$$
$$[\text{colloid } SiO_2aq.] \leftrightarrows \text{crystalloid } H_2SiO_3 \leftrightarrows 2H^{\cdot} + SiO_3''.$$

I wish to thank the Commissioners of the 1851 Exhibition for a Scholarship which has enabled me to carry out this investigation, and to express my gratitude to Professor Donnan, at whose suggestion this work was undertaken, for his constant kindly interest and advice.

The Sir William Ramsay Laboratories of Physical and Inorganic Chemistry, University College, London.

THE THERMAL DECOMPOSITION OF NITROSYL CHLORIDE[1]

BY H. AUSTIN TAYLOR AND ROY. R. DENSLOW

The purpose of the investigation reported here was to determine the effect of surface on the reaction in question. Enough has been written already to emphasise the difference between purely gas reactions and surface reactions. Even reactions to which a catalyst has not been intentionally added may be influenced by the walls of the containing vessel, probably due, as pointed out by Norrish[2], to the polar nature of glass which is so frequently used for containers. Not all reactions however, are catalytic in nature necessarily. Phosphorus trichloride and chlorine, both thoroughly dried, react at a low temperature in a wax vessel, at a rate that it is impossible to measure[3]. A large number of gas reactions have been studied by Hinshelwood and others[4] to determine their mechanism in the presence of specific catalysts. Some have been found to proceed both in the gas phase and on the surface of the catalyst or container, while a few have been found to be truly homogeneous. In a recent paper in which the well-known thermal decomposition of hydrogen iodide[5] was shown to be influenced by glass and to proceed only in part in the gas phase, it was pointed out that "attempts at a theoretical evaluation of bimolecular reaction velocities have made use in many cases of data of reactions which were assumed to be homogeneous gas reactions but which are now being shown not so." It was for this reason that the present work was undertaken.

As nitrosyl chloride is a somewhat unfamiliar substance, it may be of interest to mention briefly some of its more important properties. It is probably formed to some extent in concentrated aqua regia, but as it is easily decomposed by water, the quantity can not be very large. It is a yellowish gas, rather resembling nitrogen peroxide in appearance and having absorption bands in the orange and green[6]. The critical temperature is 163-164°C and it can be liquefied at $-5.8°$ to a blood-red liquid, which by cooling to $-61.5°$C[7] can be frozen to a red solid resembling chromic oxide in appearance. Several methods of formation are given in the literature. Two of these are more frequently used than the others; in fact most of the methods are modifications of these. The first is that of Tilden[8], and Girard and Pabst[9] which consists

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[1] Abstract from a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University.

[2] J. Chem. Soc., **123**, 3006 (1923).

[3] H. A. Taylor: J. Phys. Chem., **28**, 510 (1924).

[4] J. Chem. Soc., **123**, 2728, 2730 (1923); **125**, 393 (1924); **127**, 327, 1552 (1925); Proc. Roy. Soc., **106** A, 284 (1924).

[5] H. A. Taylor: J. Phys. Chem., **28**, 984 (1924).

[6] Magnanini: Z. physik. Chem., **4**, 427 (1889).

[7] Trautz and Gerwig: Z. anorg. Chem., **134**, 409 (1924).

[8] J. Chem. Soc., **27**, 630, 852 (1874).

[9] Bull., (2) **30**, 531 (1878).

in heating nitrosyl sulphuric acid (lead chamber crystals) with dry sodium chloride. The second is that of Gay Lussac[1] which consists in the direct combination of chlorine and nitric oxide, the reaction being represented by the equation:

$$_2NO + Cl_2 = {}_2NOCl$$

When prepared by the first method it is more likely to be contaminated by nitrogen peroxide. It will be noted that there is a rather close analogy between the gas and nitrogen peroxide. The latter can in fact be considered as nitrosyl nitrate. In a recent paper W. A. Noyes[2] reports that no binary compound of nitrogen and chlorine in which chlorine is a negative element has so far been found. In other words it seems to be impossible to replace the oxygen in nitrosyl chloride by two atoms of chlorine. Considerable work[3] has been done to determine if any other compounds of the three elements exist such for example as $NOCl_2$, $NOCl_3$, NO_2Cl etc. but there seems to be no unequivocal evidence for the existence of any of these with the possible exception of $NOCl_2$, which according to Trautz[4] is formed as an intermediate product when chlorine and nitric oxide react, but which decomposes at a comparatively low temperature. It may be mentioned also that nitric oxide is fairly soluble in liquid nitrosyl chloride but is liberated when the latter is frozen. The most important chemical property of nitrosyl chloride to be remembered in working with it, is its immediate reaction with water to form hydrochloric and nitrous acids, the latter then decomposing in the usual way.

The gas has been used by Guye[5] and others at Geneva in atomic weight work, and in their papers considerable information will be found about the details of preparation and purification as well as the physical properties. Trautz and his co-workers have studied the energetics and kinetics of the combination reaction. From the data of Trautz and Wachenheim[6], Lewis and Randall[7] have calculated the free energy change for the reaction of combination between 500° and 750°K

$$NO + 1/2\ Cl_2 = NOCl$$

as

$$\triangle F = -9100 + 14.3\ T$$

From this it will be seen that $\triangle F$ will be negative for the combination reaction at low temperatures, but will change sign as the temperature is raised, at about 636°K in fact. If we consider the decomposition of nitrosyl chloride into nitric oxide and chlorine, it is evident that we have a substance which is

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[1] Ann. Chim. Phys., (3) **23**, 203

[2] J. Am. Chem. Soc., **47**, 2159 (1925).

[3] loc. cit. also Trautz: loc. cit.

[4] Z. anorg. Chem., **136**, 1 (1925); **146**, 1 (1925).

[5] Guye and Fluss: J. Chim. Phys., **6**, 732 (1908); Boubnoff and Guye: **9**, 293 (1911); Briner and Pylkoff: **10**, 640 (1912); Wourtzel: **11**, 214 (1913).

[6] Z. anorg. Chem., **97**, 241 (1916).

[7] "Thermodynamics" (1923).

thermodynamically stable at low temperatures and unstable at high temperatures. If we consider the breaking down into its elements the reverse is true on account of the thermodynamic instability of nitric oxide.

The most accurate measurements of the kinetics of the combination at room temperatures are those of Kiss[1] in his studies of the catalytic effects of bromine and nitrogen peroxide. He agrees with Trautz in stating that the surface of the container has but little effect if any.

Experimental

Nitrosyl chloride was prepared by the method of Gay Lussac, by treating liquid chlorine with nitric oxide in excess. The chlorine was prepared in the usual manner by the action between concentrated hydrochloric acid and potassium permanganate. The gas was passed through water to remove any hydrogen chloride and the water then removed by passing through two wash bottles containing concentrated sulphuric acid and finally through about 15 cm. of phosphorus pentoxide and glass wool. The nitric oxide was made by Winkler's method[2], namely, the reaction between nitrous and hydriodic acids. To a mixture of potassium iodide and sodium nitrite covered with a little water, sulphuric acid (approximately 50 percent) was added. A rapid reaction takes place with the formation of nitric oxide and iodine. The gas was passed over a moist red phosphorus to remove any volatilised iodine, and then through sodium hydroxide solution to remove the hydrogen iodide formed and also to remove any nitrogen peroxide which might be present. The gas was dried in the same manner as was the chlorine.

The apparatus used for the preparation of the gas was similar to the one used by Trautz and Gerwig[3] in their studies of the vapor pressure of nitrosyl chloride. A suitable amount of chlorine (about 30 grams) was liquefied in the apparatus with a mixture of solid carbon dioxide and toluene. The latter which was used by Trautz, is preferable to ether as it is much less volatile. Then, taking precautions to prevent it becoming admixed with air nitric oxide was passed into the chlorine. After a short time the liquid changed from its original yellowish green color to the characteristic red of nitrosyl chloride and the color became deeper as the reaction proceeded. Care was taken to ensure that an excess of nitric acid had been used, for otherwise the product contains more than the theoretical amount of chlorine, while the excess nitric oxide can be removed by freezing and evacuating. The nitrosyl chloride so obtained was distilled twice, the second time directly into the vessel used as a reservoir throughout the experiments. During the first distillation it was passed through a tube heated to 150°C., this precaution being suggested by Trautz to decompose any dichloride which might be present. It is necessary to prepare the gas in an all-glass apparatus on account of the corrosive action on rubber.

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[1] Rec. Trav. chim., **42**, 112, 665 (1923); **43**, 68 (1924).
[2] Moser: Z. anal. Chem., **50**, 401 (1911).
[3] Z. anorg. Chem., **134**, 409 (1924).

The reaction tube which actually passed through the furnace was made of quartz and was sealed to the remainder of the apparatus, which was of Pyrex, with alundum cement and water glass. The furnace was an ordinary "multiple-unit" furnace, the ends of which were closed with thick asbestos board, with holes for the reaction tube and the thermocouple of a Hoskins pyrometer.

It was planned to study the decomposition by a dynamic method similar to that used by Taylor in the study of the decomposition of hydrogen iodide. In that work the condensed gas maintained at constant temperature, 0°C., was forced through a capillary under the constant pressure developed in the holder. The gas thus flowed at a constant rate through the reaction tube. The effluent gases were absorbed and analysed.

It was necessary, therefore to devise a method for the analysis of a mixture of nitrosyl chloride, chlorine, and nitric oxide; or if the gases were to come in contact with water, a mixture of chlorine or hypochlorous acid, nitric oxide, hydrochloric acid and nitrous acid, or the decomposition products of the latter, nitric oxide and nitrogen peroxide. This is a rather unusual mixture and a little consideration will show that none of the more obvious methods could be used. Potassium iodide solution for instance, would be affected not only by the chlorine, but also by the nitrous acid. Acidimetric methods could not be used, for acids are present from both the reactant and the resultants, not to mention the disturbing effect that the hypochlorous acid might have on any indicator. An attempt was first made to use the following procedure: to calibrate the capillary by allowing nitrosyl chloride to pass through it directly into water and to determine the chloride present by gravimetric analysis with silver nitrate. This would give a measure of the total undecomposed gas passing through the system in any specified time. As nitric oxide is so slightly soluble, it was thought that if the mixture were passed into a solution of a base, everything would be dissolved except the nitric oxide, which could be collected and measured in a eudiometer tube. Having then the total nitrosyl chloride and the nitric oxide, the composition of the mixture would be known. It was found however, that after the nitrosyl chloride had been carefully freed from dissolved nitric oxide, no measurable quantities of nitric oxide were obtained. The same results were recorded even when the gas delivery tube was surrounded by a supplementary electric heater and when the furnace itself was heated to a high temperature. This would signify either that such a small quantity had been formed that it was all dissolved, or that it had completely recombined with the chlorine before reaching the water.

Sudborough and Miller[1], by determining the vapor density, found that the dissociation of nitrosyl chloride became evident at 700°C., giving data as follows:

Temperature	Per Cent dissociated	Temperature	Per Cent dissociated
784°C	5.34	928	25.17
796	8.22	968	39.19
815	10.64	985	41.85

[1] J. Chem. Soc., **59**, 271 (1891).

If these figures could be considered reliable, it seemed likely that the recombination was the explanation of the result, and this was confirmed in the later work. For this reason another method of analysis was used, which, while having some disadvantages, seemed to be the only one available.

The total amount of nitrosyl chloride was determined in the same way as before. A standard solution of sodium arsenite, about 0.05N, free from chloride was prepared in the usual way by dissolving arsenious oxide in sodium hydroxide, neutralising the solution with sulphuric acid and then adding an excess of sodium bicarbonate to act as a buffer. This was standardised against an iodine solution of about the same concentration, which in turn was standardised against pure arsenious oxide.

A known quantity of the arsenite solution was measured in a calibrated pipette. To this, water was added and the container placed under the delivery tube for a definite time, usually ten minutes. At the expiration of that time the delivery tube was washed off and the unused arsenite titrated with the iodine solution. In this manner a measure of the free chlorine was obtained, which in turn gave a measure of the nitrosyl chloride decomposed. It was found by passing the unheated gas into the arsenite solution that the nitrous acid and other substances present were without influence on the sodium arsenite.

In order to reduce the recombination, the furnace was placed in an upright position, with the quartz reaction tube extending from it only far enough to reach the surface of the liquid in the absorbing vessel. Arrangements were made for washing off the end of the tube so that the timing of the experiment could be done with an accuracy of about one per cent. A certain amount of decomposition was now measurable, but it was small, and there was considerable deviation between the results of experiments made under the same conditions, even when the capillary was so small that only a few milligrams of gas were going through it per minute.

A few experiments were made to determine the effect of mixing oxygen with the gas before it reached the furnace. The oxygen was allowed to flow at such a rate (about 8.5 cc. per minute) that the mixture of the two gases was practically colorless before entering the furnace. At the outlet above the level of the absorbing liquid, the color was distinctly brown, due either to nitrosyl chloride, nitrogen peroxide or both. Kiss has shown that nitrogen peroxide catalyses the formation of nitrosyl chloride. It should therefore catalyse the decomposition, but it is hardly likely that that is the explanation of the effect, because at the high temperature of the furnace (700-1000°C) nitrogen peroxide is decomposed. It is probable that the oxygen lessens the time of contact of the nitrosyl chloride with the furnace, and also cuts down on the interval between leaving the furnace and reaching the absorbing liquid. The distance to be covered here was only a few centimeters but for a comparatively fast reaction like the recombination of the chlorine and nitric oxide it would be sufficiently long to have a marked effect. It must also be noted that the oxygen and chlorine would be competing for the nitric oxide and the velocities of these two reactions are about the same. It was found

that a decomposition of approximately five per cent per minute in the furnace was obtained and that this was more than doubled by doubling the rate of flow of the oxygen.

Because of the complicating factors mentioned above, it was decided to substitute dry nitrogen for oxygen as a diluent. It was mixed with the nitrosyl chloride, as in the case of the oxygen, by a side tube sealed to the apparatus between the reservoir of liquefied gas and the furnace. Its rate of flow was regulated by a capillary in one of the arms of a T tube, the other arm being connected with a cylinder of compressed nitrogen, and the upright part extending down into a cylinder of concentrated sulphuric acid. By observing the head of acid corresponding with a measured volume of nitrogen, it was possible to determine the rate of flow in any experiment with sufficient accuracy. With the capillary used, it was possible to obtain rates of flow up to about 22 cc. per minute. This is about ten times the rate of flow of the nitrosyl chloride.

In the final experiments the quantity of total nitrosyl chloride going through the system was determined frequently by absorbing the gases in sodium arsenite solution, adding silver nitrate and finally nitric acid to dissolve the silver arsenite formed along with the silver chloride. The silver chloride was filtered through a Gooch crucible.

The percentage decomposition per minute in the furnace was calculated by means of the following expression:

$$\text{Percent decomp.} = \frac{100\ a\ v\ T\ (NOCl)\ (1000)\ (298)\ W + (2.9919)\ (273)\ (AgCl)\ mg}{(2.9919)\ (273)\ (298)\ (NOCl)\ m\ F\ W}$$

where the symbols have the following significance:

a No. grams of NOCl equivalent to 1 cc. of I_2 solution.
v Vol. of I_2 used to titrate excess sodium arsenite.
T Absolute Temperature of furnace
W No. of grams of AgCl obtained in m minutes
m Time of experiment in minutes (10)
g No. of cc. of N_2 at 298°K passing per minute
F Volume of tube in furnace (58 cc.)

(NOCl) and (AgCl) represent the molecular weights of the two substances and 2.9919 grams is the weight of one liter of the former at standard conditions.

The results obtained with the empty tube are given in Table I.

It was originally intended to allow the reaction to proceed in the presence of powdered glass or silica, but this proved to be impracticable in view of the position of the furnace and the upright reaction tube. To test the effect of surface, pieces of broken quartz were placed in the tube and held in position by a plug of asbestos. The increased area thus obtained cannot be estimated with any degree of accuracy. The decrease in volume of the free space was about 15 cc. and the quartz pieces were distributed from the top to the bottom of the reaction tube. The results shown in the following table are seen to be quite comparable, within the limits of experimental error, with the previous results.

TABLE I

W	v	g	T	$10^4/T$	log % decomp.	% decomp.
0.0596	0.22	18.0	971	10.30	0.4680	2.94
.0681	.25	17.5	985	10.15	.4636	2.91
.0710	.26	17.5	984	10.16	.4635	2.91
.0840	.31	19.5	985	10.15	.5157	3.28
.0676	.27	18.5	1018	9.822	.5372	3.45
.0840	.46	19.0	1020	9.804	.6919	4.92
.0629	.37	18.0	1089	9.183	.7215	5.27
.0605	.38	18.0	1086	9.209	.7479	5.60
.0634	.26	18.0	1090	9.175	.5655	3.68
.0810	.38	19.0	1106	9.041	.6599	4.57
.0810	.31	19.0	1110	9.010	.5730	3.74
.0810	.32	19.0	1113	8.985	.5875	3.87
.0684	.30	18.5	1126	8.883	.6216	4.18
.0690	.32	18.5	1123	8.904	.6452	4.42

This is shown also by some experiments conducted with a much slower rate of flow of nitrogen, namely 6 or 7 cc. per minute. At 1019°K, decompositions of 0.99 and 0.95 per cent were obtained with the empty tube and the other respectively.

TABLE II

W	v	g	T	$10^4/T$	log % decomp.	% decomp.
0.0854	0.25	19.0	1016	9.843	0.5486	3.54
.0854	.22	19.0	1018	9.822	.4940	3.12
.0854	.34	20.0	1028	9.728	.7080	5.10
.0854	.28	19.0	1025	9.757	.6017	4.00
.0854	.29	19.0	1020	9.804	.6148	4.12
.0854	.29	19.5	1079	9.269	.6496	4.47
.0854	.30	19.0	1120	8.929	.6701	4.68
.0854	.29	19.0	1122	8.913	.6562	4.53
.0854	.33	19.0	1123	8.904	.7129	5.16
.0854	.36	19.0	1123	8.904	.7506	5.64

The obvious lack of agreement in the results recorded above calls for an investigation of the errors to which the percentage decomposition as calculated from the previous expression is affected by the variables involved. It is found in general that the percentage error in the calculated result caused by a variation of any one of the quantities a, v, T, m, g, and F, is either the same or approximately the same, as the percentage error in the value of that quantity. In no case is the error multiplied. The most serious error occurs in the evaluation of the number of grams of gas decomposed, which is obtained from v, the difference between two measured volumes of iodine solution. Since it is the rate and not the equilibrium that we are measuring, it is evident that the amount of free chlorine will be small and consequently the

difference in volume of iodine solutions will be small also. It is estimated that the error in v may be as high as 12.0%. This could doubtless have been reduced somewhat by the use of weight burettes, but in the cases of slight decomposition, would still have remained high.

Discussion of Results

If it be assumed, as the work of Trautz leads us to believe, that the decomposition takes place according to a bimolecular law, the velocities can be calculated from the ordinary expression:

$$k = 1/t.\ x/a(a-x)$$

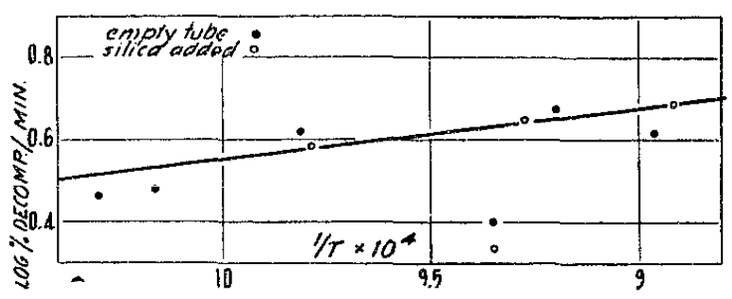


FIG. 1

by suitable substitution of the foregoing data. In the experiment at 1020°K. the following numerical result was obtained:

$$k = 5.0 \times 10^{10} \text{ cc. per mole per min.}$$

It has been pointed out above that the reverse reaction is taking place also at a rapid rate. This would raise doubt as to the validity of using the ordinary bimolecular equation. The expression for the rate of the decomposition, taking into consideration the reverse reaction, would be:

$$dx/dt = k_1(a-x)^2 - k_2(x^3/2)$$

where x is the amount of nitrosyl chloride decomposed in t minutes from an original concentration of nitrosyl chloride a. This equation cannot be readily integrated. It was decided therefore to plot the logarithm of the percentage decomposition against the reciprocal of the absolute temperature instead of the logarithm of the bimolecular constant. On account of the comparative inaccuracy of the results the mean values at the same temperature have been used. This will be seen to give over a wide range a straight line with a small slope, Fig. 1. The decompositions of the gas in the presence of the broken quartz are seen to lie on the same line.

From the slope of the line we can make an a approximation as to the heat of activation as well as the temperature coefficient. The latter has a value of about 1.025, and the former is found to be in the neighborhood of 6000 calories. The results would seem to indicate too, that the activation was not caused by the quartz, although the high temperatures necessary for reaction would probably preclude the possibility of any adsorption of nitrosyl chloride by the quartz.

If such be the case we have here another gas reaction to which the theories of activation in homogeneous systems may be applied. To take the simple

radiation theory an energy of activation of 6000 calories at these temperatures would correspond to a wave length of 4.769μ. This wave length so far as is known does not correspond with any absorption band in the spectrum of nitrosyl chloride.

Summary

1. The decomposition of nitrosyl chloride has been studied by a dynamic method between the temperatures 700° and 900°C. the rapidity of the reverse reaction being overcome by increasing the rate of flow of the gas by diluting with nitrogen.

2. The effect of an increased surface of reaction has been studied and shown to be negligible within the limits of experimental error.

3. The temperature coefficient and energy of activation appear to have values of 1.025 and 6000 calories respectively.

New York, N. Y.

THE APPARENT VISCOSITY OF COLLOIDAL SOLUTIONS

BY EMIL HATSCHEK

In a recent paper[1] McBain advances a conception of the structure of sols of nitro cotton which he summarizes as follows: "This conception shows clearly how apparent viscosity of various solutions of nitro cotton is to be explained. It is due to the presence of loose ramifying aggregates of micelles. The best solvents are those in which dismemberment proceeds furthest through solvation at the various points of affinity. Poorer solvents are those in which dismemberment is less complete and the apparent viscosity therefore much higher." McBain further assumes a general connexion between this structure and the elasticity of sols: "I venture to suggest that the presence of elasticity in a colloidal solution is a specific positive test for the presence of ramifying aggregates."

The term "elasticity" in this connexion can mean only elasticity towards shear or, to employ the usual term, rigidity (absent in normal liquids), since volume elasticity, i. e. resistance to a reduction of volume, is a common property of all liquids, whether sols or homogeneous.

The experimental data, on which these conceptions are partly based, more particularly the results of numerous viscosity determinations carried out in the ordinary capillary viscometer, are given in a paper by McBain, C. E. Harvey and L. E. Smith.[2] The summary of this paper also postulates a structure consisting of ramifying aggregates and adds: "The above theory, if correct, should be applicable throughout the whole subject of colloids."

Since these views naturally command attention, and since they have been quoted as if they were fully established,[3] it seems desirable to examine what the evidence for them actually is. There appears to be no record of such aggregates having been observed ultramicroscopically in nitro cotton sols, nor in many other highly viscous sols, like those of rubber, dyes like Cotton Yellow, or of gelatin and agar at suitable temperatures. The value of this negative evidence must, of course, not be overrated, since most sols of this type do not show differentiated particles at all. All the more importance must therefore be attached to observations on a sol, the particles of which *can* be made visible, *exhibiting high viscosity culminating even in gelation without aggregation or even mutual approach of the particles.* The aged ferric hydroxide sols investigated by E. Schalek and A. Szegvari[4] are the case in point. These sols, on the addition of electrolytes, set to gels, which can be transformed back into sols by mere shaking; the sols thus formed gelate again spontaneously, and this cycle can be repeated indefinitely, the gelation time remaining approxi-

[1] J. Phys. Chem., **30**, 239 (1926).
[2] J. Phys. Chem., **30**, 312 (1926).
[3] Bancroft: J. Phys. Chem., **30**, 1152 (1926).
[4] Kolloid-Z., **33**, 326 (1923).

mately constant. The particles are made visible by using Szegvari's "azimuth stop" with the cardioid condenser and, not being spherical, are seen only in definite orientations towards the axis of illumination and that of the microscope, so that they scintillate while in Brownian motion. When the particles come to rest, this scintillation ceases, and the process of gelation can therefore be followed with the ultramicroscope, as well as the process of liquefaction or re-solation, which pressure on the cover glass is sufficient to produce. The authors describe their observations as follows:

"If such a preparation is observed for a period of some length (which is of the same order as the time of gelation measured macroscopically), we can observe that *the scintillations gradually become feebler*, until after some time all visible movement has ceased. We are therefore observing the solidified gel. What seems most remarkable is that, apart from the cessation of the motion, *no difference at all compared with the sol state can be perceived.* There is, more especially, no trace of any formation of secondary particles; *the particles are the same mean distance from one another as in the liquid state.*" (NB. The italics throughout are those of the original).

This instance, in which the optical evidence seems complete, appears sufficient to demonstrate that gelation, and *a fortiori* the great rise in viscosity which precedes it, is possible without the formation of any aggregates whatever, whether ramifying or otherwise. The ferric hydroxide sol is quite generally considered to be hydrated and though it is not strictly a neutral sol, the latter point is immaterial in view of McBain's conditional claim that his conception is applicable to all colloids.

Schalek and Szegvari do not attempt to explain how gelation comes about without approach of the particles, nor will such an attempt be made here. It may however be worth mentioning that in a sol with optical properties very similar to those of the ferric hydroxide sol, viz. the well-known vanadium pentoxide sol, ultramicroscopic observation (by Zocher[1]) leaves no doubt that during coagulation the (rodlike) particles actually aggregate with mutual contact. This sol does not form gels, and the slow increase in viscosity during ageing is not accompanied by an aggregation.

Schalek and Szegvari have also determined, in the Hess pressure viscometer, the viscosity of their ferric hydroxide sol at different shear gradients and have found it to vary with the latter. They discuss the question whether such a variation is necessarily evidence of rigidity; in this connexion it is significant that Freundlich and Seifriz,[2] using the fairly conclusive method of micromanipulation, could not detect elasticity in a similar sol 10 years old.

A short reference to the rigidity of sols is made necessary by McBain's suggestion, quoted above, that "the presence of elasticity in a colloidal solution is a specific positive test for the presence of ramifying aggregates." Since McBain assumes this structure in nitro cotton sols, the inference is reasonable, or indeed inevitable, that he is convinced of having demonstrated elastic properties in these systems.

[1] Z. physik. Chem., **98**, 293 (1921).
[2] Z. physik. Chem., **104**, 233 (1923).

It does not appear from his paper on what evidence he relies. If it should be the variation of viscosity with shear gradient, he would be in the excellent company of authors like Freundlich and his collaborators,[1] who have investigated a large number of sols by the only theoretically correct method, viz. in a correctly designed concentric cylinder apparatus. Freundlich indeed has explicitly raised the question whether variable viscosity is conceivable apart from elastic properties. This question seems to be completely answered by the results obtained in 1916 by Edith Humphrey and E. Hatschek,[2] who demonstrated in the cylinder apparatus that *suspensions of rigid particles in a normal liquid* exhibited the same variation of viscosity with shear gradient as do lyophil sols. This result has been very generally overlooked, and the present writer and R. S. Jane have accordingly repeated and extended these determinations and have re-published them recently.[3]

McBain, indeed, quotes the earlier paper by Humphrey and Hatschek. If he relies on variable viscosity as evidence of elasticity their result places him in an obvious dilemma: he can either explain it by assuming that a few per cent of starch grains in an organic liquid impart rigidity to it, in which case rigidity is possible without ramifying aggregates; or he can admit that variable viscosity may be due to other causes besides rigidity, in which case the variable viscosity of nitro cotton sols is obviously no proof that they possess elastic properties.

As already emphasized, McBain does not anywhere explain how elastic properties in nitro cotton sols are demonstrated. In the absence of such data it seems difficult to accept his postulated connexion between a hypothetical structure and unproved elastic properties as evidence of either.

It may be added that the existence of rigidity in liquids can be demonstrated, and even the modulus be determined, by strict physical methods, so that there is no reason for relying on questionable inferences. The elegant method developed by T. Schwedoff in 1889 has recently been used by E. Hatschek and R. S. Jane[4] for an extensive investigation of typical sols, which incidentally brings out the enormous difficulty of establishing any connexion between viscosity and even a strictly defined elastic constant.

McBain advances a number of chemical considerations in support of his hypothesis of ramifying aggregates, among them one referring to a substance with which the present writer is rather more familiar than with nitro cotton: "Unpublished work by Salmon and Manning explains the action of urea in depriving gelatin of its power to set to a jelly, combination of the urea with the gelatin replacing the usual linking up of the terminal amino and carboxyl groups." A great many substances, e. g. potassium iodide, ammonium thiocyanate, calcium chloride, sodium salicylate, etc., in suitable concentrations also prevent the setting of gelatin, and presumably do so without chemical combination, as the sols again set to jellies when the salts are dialysed

[1] Freundlich, Neukircher and Zocher: Kolloid-Z., **38**, 43, 48 (1926).
[2] Proc. Phys. Soc. London, **28**, 274 (1916).
[3] Kolloid-Z., **40**, 53 (1926).
[4] Kolloid-Z., **39**, 300 (1926).

out. An effect on the linking of the terminal groups of gelatin becomes even more improbable, when it is remembered that potassium iodide and ammonium thiocyanate have exactly the same effect on sols of agar, with a totally different constitution. The combination of urea with gelatin, to put the matter plainly, is no longer gelatin, and the fact that this new body does not gelate cannot throw any light on the mechanism of gelation in unaltered gelatin.

While it is thus difficult to see any positive evidence of the existence of ramifying aggregates, and while high viscosity and even gelation are demonstrably possible without this structure, the hypothesis would still be entitled to consideration on the ground that it explained the high viscosity of sols like those of nitro cotton (or, say, of rubber) much better than any other. And of course McBain takes the view that it does so. He first insists on the inadequacy of the Einstein formula, which seems a little irrelevant, as no competent worker has ever applied it to sols exhibiting 50 to 100 times the viscosity of the dispersion medium, and conforming in no single particular to the assumptions on which the formula is based.

McBain further criticizes the present writer's view which, very briefly, is that the disperse phase in the sols under discussion consists of aggregates that have taken up a great part of the dispersion medium by a process analogous to that of swelling in bulk and that these swollen aggregates or micellae are liquid or easily deformable. The view (though this is immaterial) is practically that of Naegeli, which McBain has advocated since about 1920; the only additional assumption is that of easy deformability. Whether the process by which the micellae take up liquid is "true" solvation is quite immaterial. If the micellae are assumed of equal size and simple shape, e. g. tending to be spherical but so crowded that they have to be polyhedral, the cube root formula quoted by McBain can be deduced, which is more conveniently written:

$$\eta' = \eta \frac{1}{1 - \sqrt[3]{\varphi}}$$

where φ is the ratio: volume of disperse phase to total volume.

While this formula—necessarily—also assumes a structure, it is the simplest conceivable. Experiment has shown that the formula is even a little better than might be expected, since, as McBain points out, it expresses the viscosity of suspensions of red blood corpuscles with considerable accuracy, although these are very much larger than colloid particles, are not liquid but elastically deformable, and finally are not polyhedral, but of a peculiar shape which might give pause even to an enterprising mathematician.

It is obvious that, as φ approaches unity, the viscosity grows very rapidly; conversely, in a system with high viscosity the disperse phase must occupy practically the whole volume or, in other words, must have taken in practically the whole of the dispersion medium. McBain considers this view quite

untenable and disposes of it, as far as nitro cotton is concerned, by the statement: "We know from direct sorption experiments that nitro cotton does not take up more than its own weight of solvent."

While, of course, fully accepting this statement, one must regret that no details whatever are given of experiments to which such crucial importance is attached. To appreciate what bearing on the point at issue they really have, it would be necessary to know whether they were made in saturated vapour or in liquid solvent, and the nature of the latter; more particularly whether it was one in which nitro cotton ultimately disperses, e. g. acetone, or one in which it merely swells, e. g. alcohol at ordinary temperature. In the first alternative it would be essential to know how the sorption equilibrium was defined, and in the second the question arises how far the results are relevant at all, i. e. how they could bear on complete dispersion in another liquid.

Even in the absence of such information the argument from sorption can be disposed of by showing that:

1. Sorption experiments can give no clue to the magnitude of solvation and its variation with concentration;

2. There are plenty of substances which take up quite enough solvent to account for the volume of disperse phase required by the formula, and

3. In one, carefully investigated case a definite parallelism exists between the amounts taken up by the gel in swelling in different solvents, and the solvation or imbibition calculated from the viscosities of sols in the same solvents.

1. A case of true hydration will serve to prove this thesis. A. W. Porter[1] has calculated from Morse's and from Lord Berkeley's data on osmotic pressure the hydration numbers, i. e. the number of molecules of water associated with one molecule of sugar and thus withdrawn from the solvent. The values for two concentrations, (weight-molar) used by both investigators are given in Table I; Morse's cover a temperature range from 0° to 60°, while Berkeley's refer to 0° only:

TABLE I

Hydration of Sugar at Weight-Molar Concentrations

(Morse)

Conc.	0°	10°	20°	30°	40°	50°	60°
0.1	53	43	45	3	6.9	8.8	11.5
0.9	5.5	5.8	5.8	5.4	5.0	4.4	3.3

(Berkeley)

0.1	14
0.9	5.3

Porter adds the following comments: "Both sets agree in giving diminishing hydration with increasing concentration. In other respects the agreement is not too close; but it must be remembered that in dilute solutions in particular the degree of hydration has an exceedingly small influence on the pressure.

[1] Trans. Faraday Soc., **13** Pt. I, 13 (1917).

"The values obtained for dilute solutions at low temperatures seem surprisingly large; but I am not aware of any argument which makes them impossible."

Most of these comments could be applied verbatim to many sols. Meanwhile (provided one agrees with Porter in ascribing the discrepancies in osmotic pressure to hydration at all) it is only necessary to put the question: how sorption experiments could conceivably lead to hydration numbers such as quoted, and to the variation with concentration and temperature, to realize the impossibility of this method of attack.

2. Everyone familiar with gelatin has come across brands which, when allowed to swell in cold water, will take up a weight of water equal to eight or ten times the original weight of dry gelatin. One gm of powdered gelatin placed in 8 or 10 gm of water will thus take up the whole of it and, at the best, leave a minute intergranular film. On warming, gelation occurs and, if the temperature is raised further, the viscosity of the sol decreases much more rapidly than that of water; the viscosity changes can be explained quite simply by decreased hydration, which, on the one hand, is exactly parallel with the behaviour of sugar in true solution, and on the other in complete agreement with what is known of the thermal changes during the swelling of gelatin gel. The viscosity of the gelatin-water system below solation temperature would be (conventionally) $= \infty$; with merely 5 per cent of the imbibed water released as a consequence of dehydration caused by warming the viscosity would be about 48 (water = 1), a perfectly probable value for an 11 or 9 per cent sol within one or two degrees of the gelation temperature.

While the water absorption during swelling thus leads to perfectly possible values for the volume of disperse phase, it is necessary to emphasize that in the case of gelatin, as in that of sugar, sorption experiments in saturated water would give no clue to the subsequent behaviour of the gel. A. G. Brotman[1] in the writer's laboratory carried out the following investigation: a quantity of gelatin leaf was allowed to swell in boiled, distilled water to saturation. The figures obtained were:

Weight of air-dry leaf	6.07 gm
Weight of saturated gel	79.5 gm
Gm of water per gm of gelatin	12.09

The saturated gel was warmed, the sol allowed to set and a portion of the gel thus obtained re-immersed in the same water, in which the first swelling had taken place; it was then allowed to swell a second time to saturation. The figures obtained were:

Weight of first "saturated" gel	31.6 gm
(Weight of dry gelatin in this 31.6 gm)	2.41 gm
Weight after 5 days' immersion	40.0 gm
Gm of water per gm of gelatin	16.5

It is obvious that sorption experiments could again give no indication of this behaviour. Quite similar results have been obtained by L. Arisz[2] in an

[1] J. Soc. Leather Trades' Chemists, **1921**, 226.
[2] Kolloidchem. Beihefte, **7**, 51 (1915).

exhaustive study of gelatin sols and gels; he draws the following conclusion: "This difference in behaviour must be traced back to the state of the gelatin in the gel, and it may be considered as a further proof that that state is not at every time completely determined by the ratio of water to gelatin."

3. Rubber provides a more interesting instance than even gelatin, partly because the viscosities produced by even small concentrations approach the high figures exhibited by nitro cotton sols, and partly because full data are available, which permit a comparison of the volume of disperse phase in a sol, i. e. the volume of solvent somehow attached to one gm of rubber, with the volumes taken up in swelling to equilibrium, both sets of figures being known for a number of solvents. E. Kirchof[1] has determined the viscosity of rubber sols in various solvents by a theoretically correct method: he used a capillary viscometer *at such pressures that the viscosity no longer varied with the pressure.* From these data he calculated the volumes of disperse phase by Hatschek's formula:

$$\varphi = \left(\frac{\eta' - \eta}{\eta}\right)^3$$

The relative viscosities (solvent = 1) and the percentage volumes of disperse phase (total volume = 100) calculated from them are given in Table II.

TABLE II

Solvent	Viscosity at the concentration of 0.5%	Viscosity at the concentration of 1.0%	Vol. of disperse phase at the concent. of 0.5%	Vol. of disperse phase at the concent. of 1.0%
Benzene	2.1	4.7	16.5	51.5
Carbon Tetrachloride	2.6	7.5	24.5	70.0
Tetrachlorethane	2.5	6.9	22.0	63.0

It will be noticed that the viscosities, and therefore the volumes of disperse phase, are throughout much higher in the Cl-substituted hydrocarbons than in benzene.

E. Posnjak[2] determined in Freundlich's laboratory the amounts of the

TABLE III

Pressure in gm per sq. cm.	Gm of liquid taken up by 1 gm of rubber			Cc of liquid taken up by 1 gm of rubber		
	C_6H_6	CCl_4	$C_2H_2Cl_4$	C_6H_6	CCl_4	$C_2H_2Cl_4$
720	5.139	—	—	5.85	—	—
1120	4.409	11.064	10.517	5.02	6.92	6.61
2120	3.278	8.466	6.785	3.73	5.29	4.26
3120	2.715	6.693	—	3.09	4.18	—
4120	—	5.885	—	—	3.63	—
5120	2.088	—	4.241	2.37	—	2.69

[1] Kolloid-Z., **15**, 30 (1914).
[2] Kolloidchem. Beihefte, **3**, 432 (1912).

same liquids taken up by rubber in swelling to equilibrium under considerable pressures. The details of the experimental arrangements need not be described here; it is merely necessary to mention that true equilibria were found. Posnjak's results are given in the first three columns of Table III; the volumes in the last three columns have been calculated from them. The pressures are pressures above atmosphere.

It will be noticed at once that *rubber swells more in the chlorine-substituted hydrocarbons than in benzene, i. e. it swells more in the solvents in which it exhibits higher viscosities.* Kirchof has compared the figures for "swelling" calculated from the viscosities by Hatschek's formula with those determined by Posnjak in the following Table IV, which shows not only qualitative, but quite remarkable quantitative agreement:

TABLE IV

	Ratio of quantities taken up in sol at concent. of		Ratio of quantities taken up in swelling Posnjak at pressures of			
	0.5%	1.0%	1120	2120	3120	5120 gm/sq. cm
CCl_4 C_6H_6	1.40	1.35	1.30	1.40	1.33	1.50
$C_2H_2Cl_4$ C_6H_6	1.33	1.22	1.12	1.15	—	1.12

These ratios, calculated on the one hand from the theoretical assumptions underlying Hatschek's formula, and on the other from actual determinations of swelling equilibria, are therefore seen to agree, excellently for the ratio carbon tetrachloride benzene, and quite reasonably for tetrachlorethane benzene; an agreement which it is impossible to regard as fortuitous.

Another point remains to be discussed. According to Posnjak one gm of rubber takes up 6.92 cc of carbon tetrachloride under a pressure of 1120 gm per sq. cm. From Table III it appears that in the 1% sol in this solvent the volume of disperse phase amounts to 70 per cent, i. e. one gm of rubber has taken up about 60 cc of solvent. This appears improbable at first sight, but if the course of the pressure-volume curves (Fig. 1) plotted from Posnjak's data is considered, the difficulty disappears, as the curves are markedly hyperbolic and the volumes imbibed rise steeply with decreasing pressure, so that at zero pressure they may assume very high values. It is not necessary either that the whole of the solvent bound by the disperse phase should be accounted for by the swelling of the micellae; these, like any other particles, are probably surrounded by a layer of less mobile liquid.[1]

In conclusion it may be useful to examine briefly McBain's attitude to the fundamental problem of variable viscosity. He insists repeatedly, in speaking of nitro cotton sols, that "the apparent viscosity is not a true viscosity," "all actual measurements gave a distinct deviation from Poiseuille's law and thus do not show a true viscosity as defined by all physicists since 1860" etc. (Incidentally it is hardly correct to say that physicists have "defined" viscosity as involving an absolute constant. What they have done is to assume the viscosity coefficient independent of the shear gradient, and to develop on this basis expressions for various types of shear. Experimental demonstration of this constancy over a really extensive range is so far available for water only).

[1] Hatschek and Jane: Kolloid-Z., 40, 53 (1926).

It is not very clear what purpose this insistence on the apparent character of the viscosity is meant to serve. McBain cannot detect "yield values," in other words, the slightest pressure produces flow, as it does in normal liquids. The "apparent" viscosity which he determines in the capillary instrument certainly has the dimensions $ML^{-1}T^{-1}$, which are those of a true viscosity. The one conclusion which is both useful and inevitable when the variable character of the viscosity is emphasized, McBain, in common with many authors on the subject, does not draw: the conclusion that single viscosity measurements at arbitrary and unknown shear gradients are an inadequate

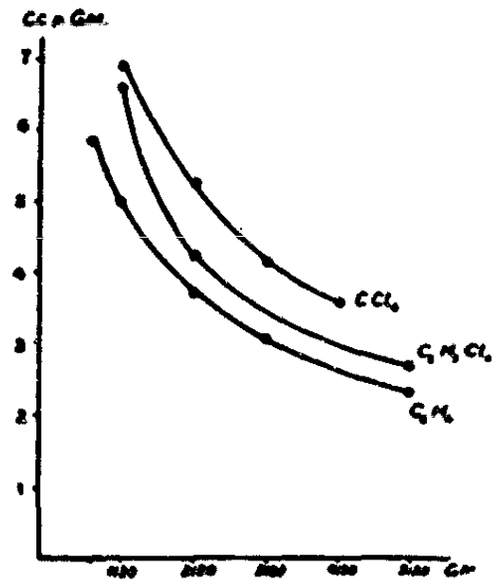


FIG. 1

foundation for theoretical deductions, especially on structure. If a physical "constant" varies with the conditions, it is obviously necessary to specify the conditions in which determinations were carried out. This position has been taken by the present writer since 1913, and in recent years has had the influential support of Freundlich.[1] If a real insight especially into structure is to be gained, complete viscosity-concentration-shear gradient surfaces must be determined, and such points as reproducibility of results, hysteresis, effect of short and prolonged shearing (which may be opposite[2]), onset of turbulence at anomalously low shear gradients, must all receive careful consideration. Finally, it would probably be sanguine to expect that the results of even so complete an investigation of any single sol, like that of nitro cotton, would be immediately "applicable throughout the whole field of colloids."

Summary

1. There is no direct evidence of the existence of ramifying aggregates in viscous sols, on the structure of which, however, the ultramicroscope in general gives little information.

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[1] "Kapillarchemie," 2nd ed., pp. 742 et seq.; Freundlich, Neukircher and Zocher: Kolloid-Z., **38**, 43, 48 (1926).

[2] Hatschek and Jane: Kolloid-Z., **38**, 33 (1926). "The Viscosity of Ammonium Oleate Solutions."

2. There is direct ultramicroscopic evidence that high viscosity and even gelation may be exhibited by a sol without aggregation and without even mutual approach between the particles.

3. Sorption experiments cannot afford information regarding the degree of hydration in true or colloidal solution and its variation with concentration.

4. Consideration of the amounts of liquid taken up by gelatin or by india rubber during swelling shows that the volumes of disperse phase postulated by Hatschek's formula are not impossible or even improbable.

5. The behaviour of rubber in various solvents has been investigated. Solvents in which rubber swells more produce more viscous sols than those in which it swells less, in strict accordance with Hatschek's assumptions and in quantitative agreement with his formula.

6. If the viscosity of a given sol varies with the shear gradient, single measurements at arbitrary and unknown shear gradients have no theoretical value, least of all as a foundation for hypotheses regarding structure.

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THE PARTIAL MOLAL VOLUMES OF WATER AND SALT IN SOLUTIONS OF THE ALKALI HALIDES*

BY VICTOR K. LAMER AND T. H. GRONWALL

In the course of a research on the extension of the Debye-Hückel theory of strong electrolytes to concentrated solutions, it was found necessary to establish empirical formulas in terms of the molality m for the partial molal volumes $\partial V/\partial n_o$ of water, and $\partial V/\partial n$ of salt, for the solutions of the alkali halides, the calculations being based on the density measurements of Baxter and Wallace.[1] The empirical formulas[2] are

$$\begin{aligned} &\text{water:} \quad \partial V/\partial n_o = a_o + a_2 m^2 + a_3 m^3 + a_4 m^4, \\ &\text{salt:} \quad \partial V/\partial n = b_o + b_1 m + b_2 m^2 + b_3 m^3, \end{aligned} \tag{1}$$

and Tables I and II give the coefficients in these formulas for the fifteen alkali halides, each at the temperatures 0°, 25° and 50.04°. The third column in the tables gives the value of m at the highest experimental point used in computing the coefficients, and extrapolation by means of the formulas beyond this value of m is not advisable.

Fig. 1 gives the graphs of the partial molal volume of the salt at 25°, computed from Table II. The formulas are derived as follows: Let V be the volume of the solution containing n_o mols of water and n mols of salt; then the molality m is given by

$$m = 55.5081\ n/n_o, \tag{2}$$

and the volume y of solution containing one mol of water by

$$y = V/n_o \tag{3}$$

From (2) it follows that

$$\frac{\partial m}{\partial n_o} = -\frac{m}{n_o}; \quad \frac{\partial m}{\partial n} = \frac{55.5081}{n_o}, \tag{4}$$

and from (3) and (4)

$$\frac{\partial V}{\partial n_o} = \frac{\partial (n_o y)}{\partial n_o} = y + n_o \frac{dy}{dm}\frac{\partial m}{\partial n_o} = y - m\frac{dy}{dm},$$

$$\frac{\partial V}{\partial n} = \frac{\partial (n_o y)}{\partial n} = n_o \frac{dy}{dm}\frac{\partial m}{\partial n} = 55.5081\frac{dy}{dm} \tag{5}$$

Now m and y may be computed directly from the volume V of solution and weights of water and salt measured by Baxter and Wallace. A curve of the fourth degree

$$y = A_o + A_1 m + A_2 m^2 + A_3 m^3 + A_4 m^4 \tag{6}$$

*Contribution from the Chemical Laboratories of Columbia University, No. 527.

[1] G. P. Baxter and C. C. Wallace: J. Am. Chem. Soc., 38, 70 (1916).

[2] Lewis and Randall ("Thermodynamics," (1923)) give a number of ingenious graphical methods for calculating partial molal volumes and discuss their thermodynamic utility.

TABLE I

Partial molal volumes of water

Coefficients in the formula

$\partial V/\partial n_o = a_o + a_2 m^2 + a_3 m^3 + a_4 m^4$

m = number of mols of salt per 1000 g. H_2O

Salt	Temperature Degrees C	Limit of Validity m	a_o	a_2	a_3	a_4
LiCl	0.00	8.00	18.018	−0.025 77	+0.008 146	−0.000 7491
	25.00	19.52	18.068	−0.015 43	+0.002 784	−0.000 1179
	50.04	19.71	18.233	−0.015 45	+0.002 768	−0.000 1174
LiBr	0.00	7.91	18.018	−0.023 18	+0.008 069	−0.000 7652
	25.00	7.98	18.068	−0.015 73	+0.005 290	−0.000 4743
	50.04	8.06	18.233	−0.015 95	+0.005 809	−0.000 5542
LiI	0.00	10.51	18.018	−0.018 99	+0.005 783	−0.000 4212
	25.00	12.11	18.068	−0.012 67	+0.004 478	−0.000 3176
	50.04	12.30	18.233	−0.012 22	+0.004 512	−0.000 3181
NaCl	0.00	5.72	18.018	−0.044 11	+0.015 689	−0.001 8766
	25.00	5.79	18.068	−0.028 98	+0.011 134	−0.001 4241
	50.04	5.86	18.233	−0.029 15	+0.013 305	−0.001 8347
NaBr	0.00	6.38	18.018	−0.040 47	+0.014 047	−0.001 5637
	25.00	6.47	18.063	−0.024 67	+0.009 129	−0.001 0535
	50.04	6.56	18.233	−0.012 52	+0.002 280	−0.000 1201
NaI	0.00	9.33	18.018	−0.032 69	+0.008 186	−0.000 6193
	25.00	9.50	18.068	−0.018 33	+0.005 556	−0.000 4656
	50.04	9.68	18.233	−0.013 18	+0.004 568	−0.000 3964
KCl	0.00	3.71	18.018	−0.066 79	+0.032 052	−0.004 9517
	25.00	3.74	18.068	−0.038 14	+0.017 662	−0.002 8059
	50.04	3.78	18.233	−0.033 62	+0.014 858	−0.002 2361

TABLE I (Continued)

Salt	Temperature Degrees C	Limit of Validity m	a_0	a_2	a_3	a_4
KBr	0.00	2.49	18.018	−0.035 68	+0.016 183	−0.004 2146
	25.00	5.59	18.068	−0.026 13	+0.010 401	−0.001 3456
	50.04	5.66	18.233	−0.021 25	+0.006 397	−0.000 5711
KI	0.00	7.57	18.018	−0.035 10	+0.010 242	−0.000 9468
	25.00	7.69	18.068	−0.022 15	+0.008 238	−0.000 8811
	50.04	7.82	18.233	−0.018 30	+0.007 692	−0.000 8527
RbCl	0.00	3.66	18.018	−0.017 08	−0.018 180	+0.006 6888
	25.00	3.41	18.068	−0.028 52	+0.010 027	−0.001 4133
	50.04	3.73	18.233	−0.043 42	+0.032 794	−0.007 2131
RbBr	0.00	2.88	18.018	−0.068 49	+0.065 456	−0.019 2078
	25.00	2.90	18.068	−0.025 11	+0.006 258	+0.000 1631
	50.04	2.94	18.233	−0.047 89	+0.050 292	−0.014 4810
RbI	0.00	3.24	18.018	−0.070 28	+0.065 918	−0.017 8560
	25.00	3.27	18.068	−0.020 36	+0.008 554	−0.001 5321
	50.04	3.31	18.233	−0.018 43	+0.008 713	−0.001 3442
CsCl	0.00	5.26	18.018	−0.042 60	+0.015 871	−0.001 9702
	25.00	5.32	18.068	−0.032 34	+0.014 309	−0.001 9945
	50.04	5.38	18.233	−0.029 60	+0.013 472	−0.001 8947
CsBr	0.00	3.60	18.018	−0.059 18	+0.041 741	−0.009 1084
	25.00	5.31	18.068	−0.031 57	+0.012 762	−0.001 5574
	50.04	5.39	18.233	−0.020 80	+0.007 147	−0.000 8003
CsI	0.00	1.57	18.018	−0.027 85	−0.039 263	+0.037 3619
	25.00	3.52	18.068	−0.039 13	+0.035 160	−0.008 2403
	50.04	3.57	18.233	−0.049 88	+0.055 169	−0.014 0453

TABLE II

Partial molal volumes of salt.

Coefficients in the formula

$\partial V/\partial n = \bar{V} = b_o + b_1 m + b_2 m^2 + b_3 m^3$

m = number of mols of salt per 1000 g. H_2O

Salt	Temperature Degrees C	Limit of Validity m	b_o	b_1	b_2	b_3
LiCl	0.00	8.00	+16.03	+2.861	−0.6782	+0.055 44
	25.00	19.52	+17.59	+1.713	−0.2318	+0.008 72
	50.04	19.71	+17.47	+1.715	−0.2304	+0.008 69
LiBr	0.00	7.91	+22.49	+2.573	−0.6718	+0.056 63
	25.00	7.98	+24.47	+1.746	−0.4404	+0.035 11
	50.04	8.06	+24.76	+1.771	−0.4836	+0.041 02
LiI	0.00	10.51	+32.94	+2.108	−0.4815	+0.031 18
	25.00	12.11	+35.75	+1.407	−0.3729	+0.023 50
	50.04	12.30	+36.71	+1.356	−0.3757	+0.023 54
NaCl	0.00	5.72	+13.44	+4.897	−1.3063	+0.138 89
	25.00	5.79	+17.22	+3.217	−0.9270	+0.105 40
	50.04	5.86	+18.40	+3.236	−1.1078	+0.135 78
NaBr	0.00	6.38	+19.85	+4.492	−1.1696	+0.115 73
	25.00	6.47	+24.10	+2.739	−0.7601	+0.077 97
	50.04	6.56	+26.12	+1.390	−0.1898	+0.088 90
NaI	0.00	9.33	+30.44	+3.629	−0.6816	+0.045 83
	25.00	9.50	+35.48	+2.035	−0.4626	+0.034 46
	50.04	9.68	+37.92	+1.463	−0.3804	+0.029 34
KCl	0.00	3.71	+22.92	+7.415	−2.6687	+0.366 48
	25.00	3.74	+27.02	+4.234	−1.4706	+0.207 67
	50.04	3.78	+28.08	+3.732	−1.2371	+0.165 50

TABLE II (Continued)

Salt	Temperature Degrees C	Limit of Validity m	b_0	b_1	b_2	b_3
KBr	0.00	2.49	+30.90	+3.961	−1.3474	+0.311 92
	25.00	5.59	+34.46	+2.900	−0.8660	+0.099 59
	50.04	5.66	+35.86	+2.359	−0.5326	+0.042 27
KI	0.00	7.57	+41.38	+3.897	−0.8527	+0.070 08
	25.00	7.69	+45.83	+2.459	−0.6859	+0.065 21
	50.04	7.82	+47.92	+2.031	−0.6404	+0.063 11
RbCl	0.00	3.66	+29.92	+1.897	+1.5137	−0.495 04
	25.00	3.41	+32.57	+3.166	−0.8349	+0.104 60
	50.04	3.73	+33.37	+4.821	−2.7305	+0.533 85
RbBr	0.00	2.88	+35.29	+7.604	−5.4500	+1.421 58
	25.00	2.90	+39.47	+2.788	−0.5210	−0.012 07
	50.04	2.94	+40.52	+5.316	−4.1874	+1.071 75
RbI	0.00	3.24	+45.84	+7.802	−5.4885	+1.321 54
	25.00	3.27	+51.03	+2.261	−0.7122	+0.113 39
	50.04	3.31	+53.12	+2.046	−0.7255	+0.099 48
CsCl	0.00	5.26	+36.49	+4.729	−1.3215	+0.145 81
	25.00	5.32	+39.81	+3.590	−1.1914	+0.147 61
	50.04	5.38	+40.98	+3.286	−1.1217	+0.140 23
CsBr	0.00	3.60	+42.66	+6.570	−3.4754	+0.674 12
	25.00	5.31	+46.46	+3.505	−1.0626	+0.115 27
	50.04	5.39	+48.37	+2.309	−0.5950	+0.059 23
CsI	0.00	1.57	+53.77	+3.091	+3.2691	−2.765 18
	25.00	3.52	+58.09	+4.344	−2.9275	+0.609 87
	50.04	3.57	+60.00	+5.538	−4.5935	+1.039 50

is then fitted to the computed points. Doing this by the method of least squares, besides being extremely laborious, would be of doubtful value, since the number of experimental points is small. The curve was therefore simply passed through the five experimental points corresponding to $m = 0$ (the value of y being computed from the volume of 1 g. of water,)[1] and the lowest and the three highest m-values of Baxter and Wallace. This curve fits the intermediate points very well, as is seen from Table III, where the second column contains the experimental y-values and the third the difference between this and the y computed from equation (6):

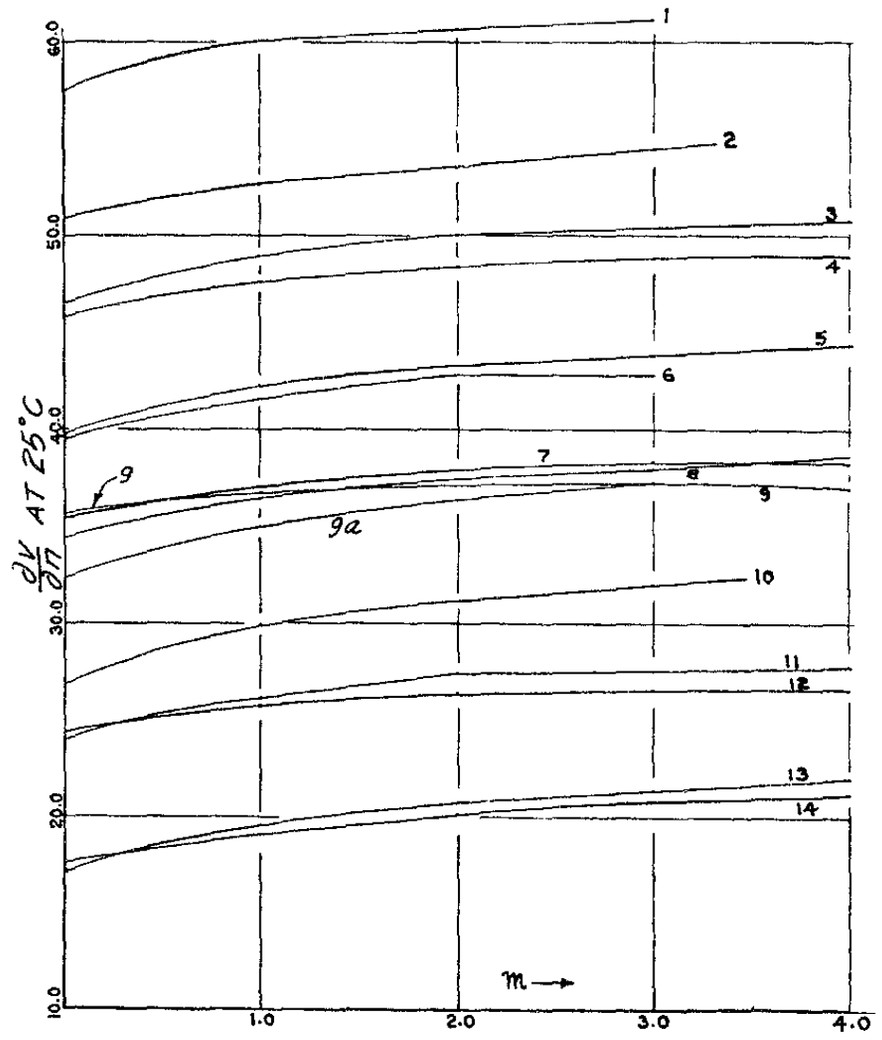


FIG. 1

1 = CsI; 2 = RbI; 3 = CsBr; 4 = KI; 5 = CsCl; 6 = RbBr; 7 = NaI; 8 = KBr; 9 = LiI; 9a = RbCl; 10 = KCl; 11 = NaBr; 12 = LiBr; 13 = NaCl; 14 = LiCl

In one case only (KCl at 0°), the differences are slightly greater than these; in all other cases they are considerably smaller. Let m_i, y_i ($i = 0, 1, 2, 3, 4$) be five points, $f(m) = (m - m_0)(m - m_1) \ldots (m - m_4)$ and $f_i(m) = f(m)/(m - m_i)$; then the fourth degree curve passing through the five points is given by Lagrange's interpolation formula

$$y = \sum_{i=0}^{4} y_i \frac{f_i(m)}{f_i(m_i)} \qquad (7)$$

[1] Landolt and Börnstein: Physikalisch-Chemische Tabellen, p. 43 (1912).

and the coefficients A_0 . . ., A_4 are found by multiplying out the products and collecting terms.[1] The coefficients in (1) are then found at once by substituting (6) in (5). To form an estimate of the error in $\partial V/\partial n$, for instance, due to errors $\triangle y_1$, . . ., $\triangle y_4$ in the experimental values of y_1, . . . , y_4 we observe that the error in y is, according to (7)

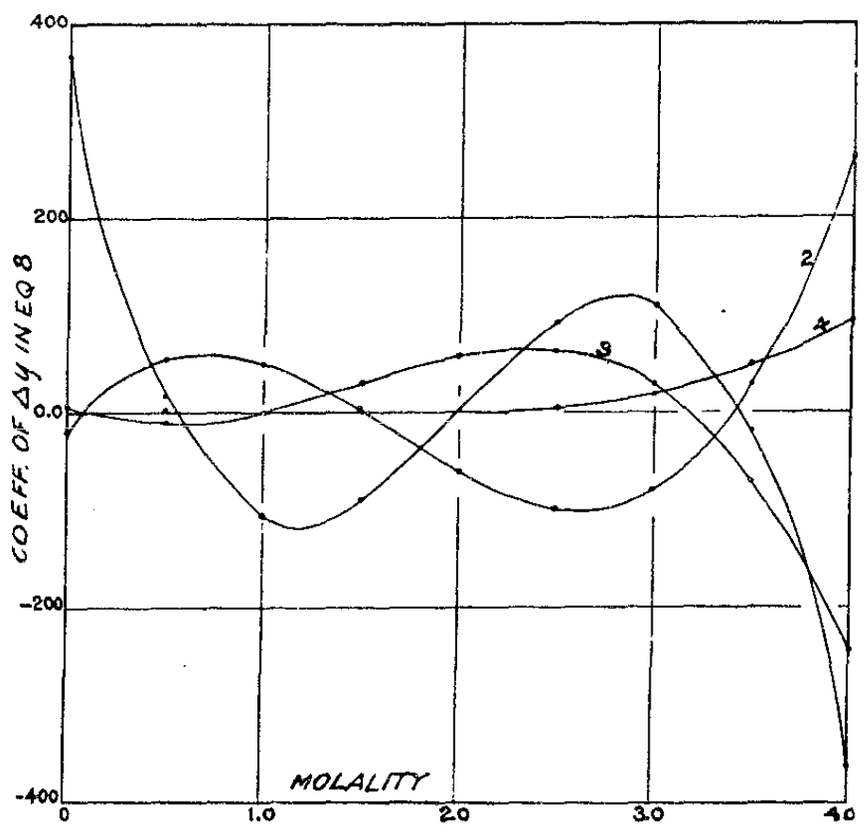


FIG. 2

Relative effect of an error in the experimental values of y (the volume of solution containing one mol of water) at m = 0.2, 1.5, 2.5, and 4.0, respectively, which correspond approximately to the points used in constructing Table III, upon the calculated value of $\partial V/\partial n$ at various molalities.

TABLE III

KCl at 25°

m	y exp.	y exp. −y calc.
0.0000	18.0683	0.0000
0.1668	18.1505	0.0000
0.2742	18.2052	+0.0008
0.3383	18.2381	+0.0011
0.6839	18.4188	+0.0024
0.9464	18.5578	+0.0015
1.7670	19.0044	0.0000
2.4694	19.4045	0.0000
3.7470	20.1454	0.0000

[1] The actual computation was done by the "divided difference formula," which is easier to handle numerically; see Whittaker and Robinson: "Calculus of Observations," (1924).

$$\Delta y = \sum_{i=1}^{4} \Delta y_i \frac{f_i(m)}{f_i(m_i)}$$

and consequently, by (5)

$$\Delta\left(\frac{\partial V}{\partial n}\right) = \sum_{i=1}^{4} \Delta y_i \cdot 55.5081 \frac{f'_i(m)}{f_i(m_i)} \qquad (8)$$

In Fig. 2, the coefficients of $\Delta y_1 \ . \ . \ ., \Delta y_4$ in (8) are plotted against m and marked 1, 2, 3, 4; they were calculated for $m_0 = 0$, $m_1 = 0.2$, $m_2 = 1.5$, $m_3 = 2.5$, $m_4 = 4.0$ which correspond roughly to the five points used in constructing Table III. Fig. 2 shows, for instance, that at $m = 0$ as well as at $m = 4$, an error in y, contributes an error in $\partial V/\partial n$ 366 times as large.

If the experimental error in y_1 does not exceed a unit in the sixth significant figure, then the error due to it in $\partial V/\partial n_0$ should not exceed four units in the fourth significant figure. Similar estimates may be made of the errors due to errors in y_2, y_3 and y_4, and the corresponding errors in $\partial V/\partial n_0$ and $\partial V/\partial n$, with the result that the maximum error to be expected in using Tables I and II is two units in the fifth significant figure of $\partial V/\partial n_0$, and five units in the fourth significant figure of $\partial V/\partial n$, i. e., ± 0.05 cc. In some of the determinations of the volume of the solutions, the error may be at least five parts per million, so that a probable error of 0.20 cc. in $\partial V/\partial n$ is possible.

A check upon the accuracy of the results for practical purposes can be obtained by considering the differences between the values of the partial molal volumes of the salt $\partial V/\partial n = \bar{V}$ at infinite dilution.

TABLE IV

Differences in the Partial Molal Volumes of the Alkali Halides at Infinite Dilution

M	$\bar{V}_{MBr} - \bar{V}_{MCl}$			$\bar{V}_{MI} - \bar{V}_{MBr}$		
	0.00°C.	25.00°C.	50.04°C.	0.00°C.	25.00°C.	50.04°C.
Li	6.46	6.88	7.29	10.45	11.28	11.95
Na	6.41	6.88	7.72	10.59	11.38	11.80
K	(7.98)	(7.44)	7.78	10.48	11.37	12.06
Rb	(5.37)	6.80	7.15	10.55	11.56	12.60
Cs	6.17	6.65	7.39	(11.11)	11.63	11.63
Average	6.35	6.95	7.47	10.52	11.44	12.01
X	$\bar{V}_{NaX} - \bar{V}_{LiX}$			$\bar{V}_{KX} - \bar{V}_{NaX}$		
Cl	−2.59	−0.37	+0.93	(+9.48)	(+9.80)	(+9.68)
Br	−2.64	−0.37	+1.36	+11.05	+10.36	+9.74
I	−2.50	−0.27	+1.21	+10.94	+10.35	+10.00
Average	−2.58	−0.31	+1.17	+11.00	+10.35	+9.87
X	$\bar{V}_{RbX} - \bar{V}_{KX}$			$\bar{V}_{CsX} - \bar{V}_{RbX}$		
Cl	(+7.00)	+5.55	+5.29	6.57	6.24	7.61
Br	+4.39	+5.01	+4.66	6.37	6.99	7.85
I	+4.46	+5.20	+5.20	(7.93)	7.06	6.88
Average	4.43	5.25	+5.05	6.47	6.76	7.45

Since at infinite dilution the partial molal volume of a given anion should be independent of the cation with which it is associated, the difference

$$\overline{V}_{M\,Cl} - \overline{V}_{M\,Br}$$

should be a constant at a given temperature and should represent the difference $\overline{V}_{Cl^-} - \overline{V}_{Br^-}$

Likewise the difference $\overline{V}_{NaX} - \overline{V}_{LiX}$ should be constant and represent the difference in partial molal volumes of the sodium and lithium ions at infinite dilution.

Some of the possible combinations are assembled in Table IV. They were obtained by direct combination of the respective values of b_o in Table II.

A consideration of the data of Table IV shows that with the exception of those differences which involve KCl at 0°, 25° and 50°C. and also CsI and RbCl at 0°C. that the values for a given combination check very well, usually within one or two tenths of a cc. The values for b_o in Table III are therefore on the whole correct to within this range of variation.

Lamb and Lee[1] measured by a very ingenious and accurate method the densities of highly dilute solutions of sodium and potassium chlorides. Their data yield 10.386 at 20° C. for the difference for the partial molal volume of potassium ion minus sodium ion at infinite dilution, while our calculations for the same difference using the bromides and iodides yield respectively 10.36 and 10.35 at 25° C. The difference K—Na obtained from the respective chlorides is 9.80 or 0.55 cc. lower. As was noted above the KCl density data do not fit the empirical equation (6) as well as the other data, and after rechecking our figures we are obliged to attribute the discrepancy to an error which has crept into the density data for KCl. Since Baxter and Wallace employed the same weighed portion of KCl for many of their density determinations at the different temperatures it is possible that the source of the error may reside entirely in a single weighing.[2]

We may avoid this uncertainty and obtain a value for $\overline{V}_{KCl}$ at infinite dilution in the following way: If we grant that $\overline{V}_{NaCl}$ is correctly determined in Table II and that the difference $\overline{V}_{K^+} - \overline{V}_{Na^+}$ as given by the bromide and iodide data in Table IV is correct as seems quite certain from the check with Lamb and Lee's data, then the partial molal volume of KCl at infinite dilution should be 13.44 + 11.00 = 24.44 at 0° instead of 22.92 as indicated by the b_o value in Table II; similarly for 25° C. we find 17.22 + 10.35 = 27.57 instead of 27.02 and for 50° C. 28.27.

These calculated values may be checked in the same manner by employing the differences between the lithium and potassium series, and assuming that the b_o value for lithium chloride is correct. Table V lends further weight to the assumption that the data for KCl are incorrect.

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[1] J. Am. Chem. Soc., **35**, 1683 (1913).

[2] The coefficients b_1 and b_2 in Table II also indicate irregularities in the data for KCl, RbCl (0°) and CsI (0°). The same holds true of course for the data in Table I. Using a 3rd degree equation on the first and highest two experimental points we get 27.13 cc. as the value for KCl at 25° C. A third degree equation on the first three experimental points yields 27.15 cc. The error evidently resides in the first experimental point; namely 0.1688m of Table III.

TABLE V
$\bar{V}_{KX} - \bar{V}_{LiX}$

Anion employed	0.00°	25.00°	50.04°
Cl	(6.89)	(9.43)	(10.61)
Br	8.41	9.99	11.10
I	8.44	10.08	11.21
Average	8.42_5	10.04_5	11.15_5

The results based upon the correctness of the b_o for LiCl in Table II and the averaged values of Table V yield for $\bar{V}_{KCl}$ at infinite dilution the values 24.45_5 (0°); 27.53_5 (25°) and 28.62 (50°), which are in substantial agreement with those based upon the NaCl data.

In view of this concordance we feel that the most probable values for $\bar{V}_{KCl}$ are **24.45** (0°); **27.55** (25°) and **27.32** (50.04°) instead of the b_o values of Table II.

Adjusted values for $\bar{V}_{RbCl}$ at 0° C. based upon the results of Table VI yields 28.86 (NaCl series) and 28.88 (LiCl series) or **28.87** as the most probable value for RbCl instead of the b_o value 29.92 in Table II.

TABLE VI

X	$\bar{V}_{RbX} - \bar{V}_{NaX}$	$\bar{V}_{RbX} - \bar{V}_{LiX}$
Cl	(16.48)	(13.89)
Br	15.44	12.80
I	15.40	12.90
Average	15.42	12.85

From the bromide-iodide combination Table IV and the b_o value for CsBr we get $\bar{V}_{CsI}$ at 0° = 53.18. From the iodide-chloride combination for lithium and sodium (K, Rb and Cs cannot be used in this series) we get, using the b_o value for CsCl, $\bar{V}_{CsI}$ at 0° = 53.43.

The value 53.18 is based upon four differences and the weighted average for $\bar{V}_{CsI}$ at 0° becomes 53.26 instead of 53.77 as given in Table II.

Unfortunately the principle upon which the adjustments are based is valid only for infinite dilution, and we cannot estimate in advance how the higher coefficients in Tables I and II, which give a measure of specific effects between the ions should be adjusted.

Discussion of Results

The *interpretation of partial molal volumes* in aqueous solution is unquestionably a matter of considerable complexity, and any attempt to "explain" the values on simple assumptions must necessarily encounter difficulties. Since the values of $\bar{V}$ are almost always smaller than the corresponding molecular volumes of the solid salts, and in certain cases notably Na_2CO_3 and $MgSO_4$ even negative in value, it is necessary to assume the operation of *at least* two opposing factors; viz:

(a) The true volume of the ions;

(b) the compression of the solvent about the ion usually denoted as electrostriction.[1]

As its name indicates (b) is considered to be brought about by the attraction of the water dipoles through the electric field created by the ions, with the result that an increased density and orientation of the water molecules occurs in the immediate neighborhood of the ions.

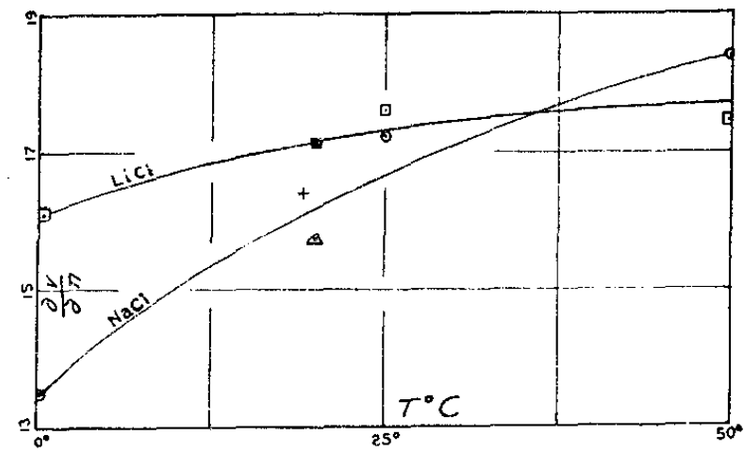


FIG. 3

Effect of temperature on the partial molal volumes of NaCl and of LiCl at infinite dilution.

○ NaCl—present investigation
△ NaCl—Lamb and Lee (20°C)
+ NaCl—Wade (18°C)—calculated by Lewis and Randall: "Thermodynamics," p. 36.
□ LiCl—present investigation
× LiCl—Lamb and Lee (20°C).

Since the data of this paper were assembled, T. J. Webb[2] has published a very interesting mathematical theory of electrostriction along the lines just sketched. He has also calculated the free energies of hydration of the alkali halides (except lithium) by considering their ions to behave as charged spheres, and compares the radii so obtained with those calculated from the data on partial molal volumes at great dilution. He obtains very plausible values for the radii and in the limited cases where the necessary data are available agreement appears to be secured between the two methods. He did not discuss the effect of temperature and it will be important to see whether the radii which he has calculated can account for the variation in partial molal volume with temperature. As Table IV shows the temperature coefficient is usually positive for the differences as written, one of the most marked temperature coefficients being given by the difference $\bar{V}_{Li^+} - \bar{V}_{Na^+}$. In Fig. 3 we have plotted the limiting values of $\bar{V}$ for LiCl and NaCl against the temperature. Calculations[3] which we have made for the "apparent" diameter of the ions "a" in the Debye-Hückel theory of electrolytes indicate that this quantity

[1] Drude and Nernst: Z. physik. Chem., **15**, 79 (1894).

[2] T. J. Webb: J. Am. Chem. Soc., **48**, 2589 (1926).

[3] Forthcoming publication. For a preliminary abstract see Science, **64**, 121 (July 30, 1926).

changes markedly with temperature, and it is possible that the so-called radii of the ions calculated by Webb may also prove to vary with the temperature, but according to his picture of ionic size it would be difficult to interpret such a variation. That arbitrary values for the ionic radii will not in themselves explain the values for all of the alkali halides is evident when we consider the lithium salts. The radius for lithium is generally given as smaller than that of sodium and consequently the electric field strength about the lithium ion should be greater with the result that a smaller value of $\bar{V}$ would be expected. As Table II and Fig. 1 show the reverse is the case at temperatures below 50° C., NaCl having a lower value at high dilution than does LiCl, and the same is true of the bromides and iodides. The curves cross above 0.5M and the expected regularity is obtained only in concentrated solution.

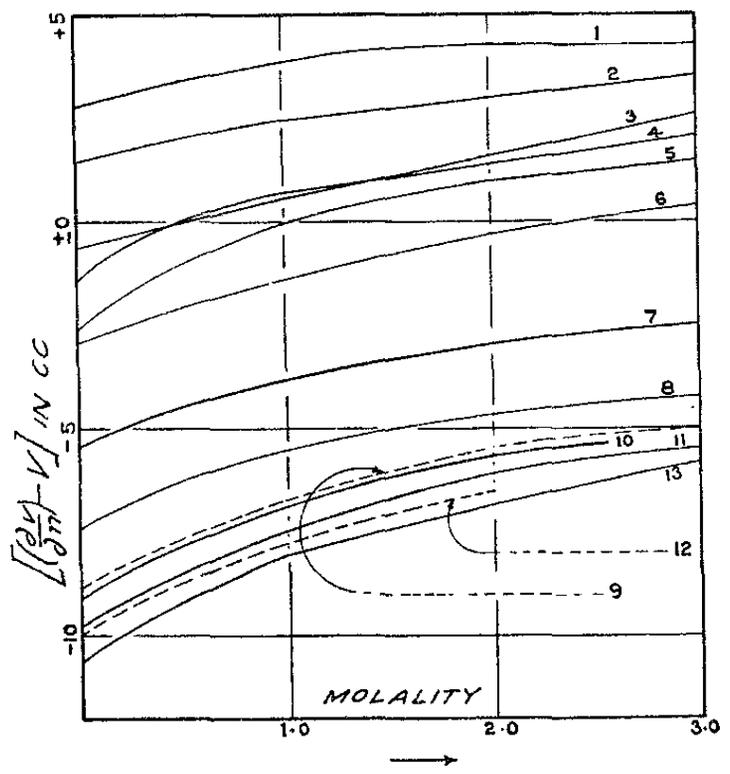


FIG. 4

1 = LiI; 2 = CsI; 3 = CsBr; 4 = LiBr; 5 = CsCl; 6 = LiCl; 7 = NaI; 8 = KI; 9 = KBr and RbI; 10 = NaBr; 11 = NaCl; 12 = RbBr; 13 = RbCl and KCl.

Lamb and Lee's results at 20° C. for infinite dilution which we give below yield the same result; namely, LiCl = 17.12_5; NaCl = 15.71_4; KCl = 26.10; NH_4Cl = 24.95. Wade's data[1] gives HCl = 17.82 at 18° C., which is even more difficult to interpret. We suggest that as the ionic size decreases factors other than the field strength at the surface of the ion become important. Thus in the extreme case of a proton (hydrogen ion) there is not sufficient surface for more than one molecule of H_2O to be compressed about it with the result that the proton is absorbed by the water molecule and the charge is distributed upon the hydronium ion H_3O^+. Lithium ion very likely behaves in a similar way, i. e., it forms a true chemical hydrate. There is much

[1] Wade: Landolt-Börnstein "Tabellen," p. 287 (1912).

evidence that the hydrogen ion exists only in this mono-hydrated form. If this is the case then we should employ the partial molal volume of hydronium chloride $[H_3O]^+ Cl^-$ which at infinite dilution equals the sum of the values for HCl and for H_2O; namely 35.87 cc. It is interesting that this value is not very different from that of the corresponding ammonium chloride; namely 34.95 cc.

It is well known that the general behavior of NH_4^+ as an alkali ion does not accord with its atomic or radical weight, which places it between lithium and sodium. Instead it resembles K^+ and Rb^+ much more closely in properties such as the solubility of the chlorplatinate and bitartrate. According to the modern physical view these properties are governed in the case of the larger ions primarily by the size of the sphere upon which the charge of the ion is distributed, and the partial molal volume of NH_4Cl which is practically identical with that of RbCl lends support to this view.

The difference between the partial molal volume and the molecular volume of the solid salt; namely $(\bar{V} - V)$ gives the change in volume which one mol of salt produces on dissolving, the composition of the solution remaining unchanged. Fig. 4 gives a plot of the values of $(\bar{V} - V)$ in terms of the molality of the solution. These values differ somewhat from the values given by Baxter and Wallace, except at infinite dilution, since their calculations give what is essentially the integral change in volume; i. e., the volume change which the salt and pure water undergo in forming a solution of a given molality. The data of Fig. 4 were calculated from the empirical expressions of Table II and in certain cases may carry the errors previously referred to.

Most striking are the values of the cesium salts and particularly the iodide which actually expands on dissolving. Baxter and Wallace have discussed this question from the standpoint of T. W. Richards' theory of the compressible atom and point out that the atoms are undoubtedly highly compressed in the solid state. Webb's calculations also indicate this since they show that the radii of the ions in solution are on the average about 0.47 Å larger than the corresponding values obtained from X-ray measurements on crystals. In regard to the position of the cesium salts in Fig. 4, it is well to point out that the atoms (ions) of these salts are arranged in the crystal in the form of a body-centered lattice, while in the case of all of the other alkali salts the arrangement is of the simple cubic or NaCl type.

Summary

1. A rapid analytical method for the calculation of the partial molal volumes of the salt and of the solvent from density determinations is described.

2. Values for the partial molal volumes of the water and of the salt at 0°, 25°, and 50° C. have been calculated for the fifteen alkali chlorides, bromides and iodides by the use of a fourth degree equation to represent the density data of Baxter and Wallace. The effect on the final result of errors in the original data are discussed.

3. There are strong indications that the density data for KCl at 0°, 25° and 50° C. and for RbCl and CsI at 0° C. may be sufficiently in error to ac-

count for certain irregular results. The values for the other salts are consistent with one another. On the basis of this consistency and the principle of the additivity of the properties at infinite dilution adjustment in the limiting values for KCl, RbCl and CsI has been made.

4. The bearing of the results and particularly the effect of temperature have been briefly discussed in the light of T. J. Webb's theory. The position of NH^+_4 ion in the alkali series is interpreted on the basis of its partial molal volume.

New York, N. Y.

DIFFUSION OF AQUEOUS SODIUM SILICATE SOLUTIONS ACROSS SEMIPERMEABLE MEMBRANES

BY PHANI BHUSAN GANGULY

From the measurements of scattering, a very marked change has been observed as the molar ratio of SiO_2 : Na_2O increased beyond 3 : 1. In the following experiments the distribution of the silicate solutions across different membranes has been investigated in the hope that more precise information as to the change in colloidal aggregates with increase of ratio, will be available. Solutions of the silicates were allowed to attain equilibrium against water. Both parchment and collodion membranes have been used. After equilibrium the respective solutions have been analysed, their osmotic pressures measured, and also their pH values ascertained. From these measurements an attempt has been made to determine the colloidal aggregations of sodium silicates, and to follow the change in the colloidal properties with change of ratio.

A parchment membrane was clamped in position in a Donnan membrane vessel. A solution of sodium silicate of known concentration was put in one compartment of the vessel, the other compartment containing distilled water. The volume of the water used was adjusted in such a way that after equilibrium, the volumes of liquid in both the compartments were about the same. To hasten the equilibrium the solutions were stirred by a current of nitrogen. The nitrogen was carefully purified from carbon dioxide, washed and dried. Before entering the membrane vessel, it passed through the bubblers A and A_1, and B and B_1. The bubblers A and A_1, contained the same silicate solutions as in the membrane vessels, whilst B and B_1, acted only as traps. Atmospheric carbon dioxide was excluded by another trap at C and C_1, attached to the exit tubes. The arrangement is shown diagrammatically in Fig. 1. A series of such vessels were set up so that they could all be stirred simultaneously. To determine the equilibrium point, solutions were drawn out from time to time and analysed. It was found that the solutions attained equilibrium in about one week's time, as was determined by the constancy of analytical results.

When collodion was used as the membrane, the membrane vessel took the form of two concentric tubes. Water was put in the outer vessel whilst the inner tube contained the silicate solutions. The volumes of liquids used were again adjusted so far as possible, so as to get the same volume of solution in both the tubes after equilibrium. The inner tube consisted of a collodion sack, which was mounted on to a glass tube. For the preparation of the collodion sack the commercial "Necol", which is a 13% solution of collodion, was used. The sack was made from the inside of a tube of the required size, care being taken to avoid the formation of air bubbles. It was found that better results could be obtained by holding this tube symmetrically inside an

outer jacket with the help of bored corks, and thereby excluding the warmth of the hand. A current of air was also drawn through the tubes to hasten the drying of the collodion. The sack was then put on to a piece of glass tube of size just big enough to allow the sack to slip on easily. In about a couple of hours the collodion sack dries a little and thus grips the tube very firmly, making a perfectly air-tight joint. To avoid the shrinking of the rest of the sack while it is drying to grip the tube, it was kept full of water. This was found to be a more satisfactory process than the usual practice of tying the sack with rubber bands or threads.

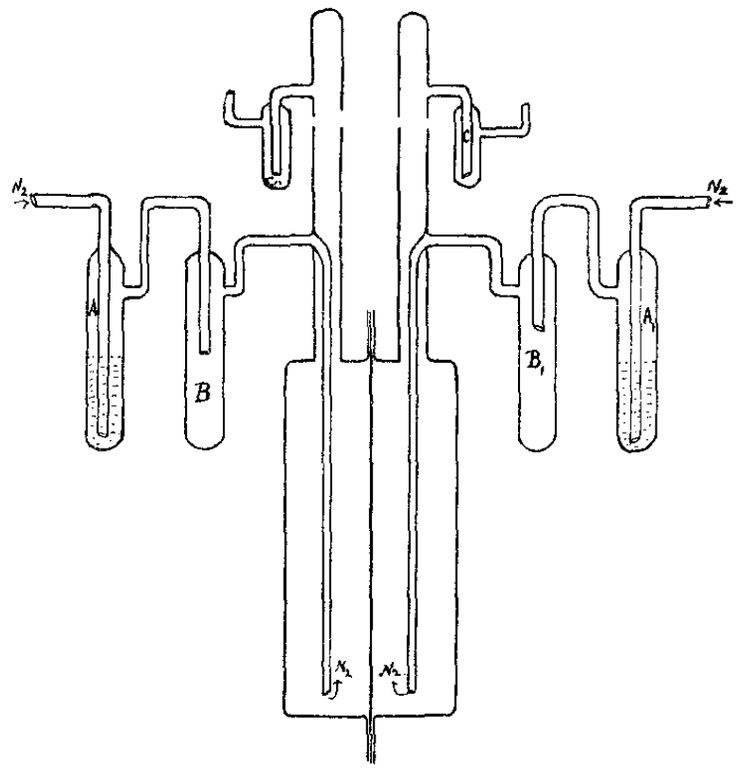


FIG. 1

No stirring was done in these cases, but sufficient time was allowed for the attainment of equilibrium, which was determined as before, by the concurrence of analytical results. After equilibrium the solutions were drawn out, their total volume and density measured, and also analysed. The silica was estimated by repeated evaporation to dryness with hydrochloric acid, and the sodium was estimated in the filtrate as sodium chloride. The experimental analytical results are given in Tables I-II.

From these tables we find that sodium silicate solutions contain considerable proportions of non-diffusible ions or combined molecules. The difference in the analytical values of SiO_2 and Na_2O for the solution H, in which the molar ratio of silica to alkali is 2 : 1, is however, quite small, showing thereby that this solution contains a correspondingly small amount of non-diffusible matter. If this solution consisted of simple ions like Na^+ and SiO_3^-, and the non-diffusible matter consisted of combined ions of the general type $[SiO_3)n]^-$, then, according to the Donnan membrane law, there should be an increase of

TABLE I

Analyses after equilibrium with parchment paper

	Molar ratio	Silicate Compartment.		Water Compartment.		Difference	
		SiO_2 gms per 100 ccs.	Na_2O gms per 100 ccs.	SiO_2 gms per 100 ccs.	Na_2O gms per 100 ccs.	SiO_2	Na_2O
A.	4.2	1.8930	0.399	1.107	0.335	.786	.064
B.	3.95	1.8024	0.4238	1.1908	0.3648	.6116	.059
C.	3.8	1.6996	0.4308	1.2942	0.3806	.4054	.0502
D.	3.3	1.6308	0.4802	1.3664	0.4548	.2644	.0254
E.	3.0	1.5254	0.5192	1.4734	0.5090	.052	.0102
G.	2.5	1.5372	0.6236	1.4752	0.6140	.062	.0096
H.	2.0	1.5074	0.766	1.4918	0.7748	.0156	−0.0088

TABLE II

Analyses after equilibrium with collodion membranes

	Molar ratio $\frac{SiO_2}{Na_2O}$	Silicate compartment		Water compartment		Difference	
		SiO_2 gms per 100 ccs.	Na_2O gms per 100 ccs.	SiO_2 gms per 100 ccs.	Na_2O gms per 100 ccs.	SiO_2	Na_2O
A.	4.2	1.1094	0.2062	0.3968	0.1624	.7126	0.0438
B.	3.95	1.0478	0.2172	0.4608	0.1748	.5870	0.0424
C.	3.8	0.9298	0.2246	0.5776	0.1834	.3522	0.0412
D.	3.3	0.8788	0.2524	0.6294	0.2176	.2494	0.0348
E.	3.0	0.7736	0.2640	0.7332	0.2524	.0404	0.0116
G.	2.5	0.7722	0.3178	0.7338	0.3022	.0384	0.0156
H.	2.0	0.7568	0.3852	0.7496	0.3896	.0072	−0.0044

silica in the silicate compartment, which should be counterbalanced by an increase of sodium in the water compartment satisfying the relation:—

$$[Na]_{sil} \times [SiO_3]_{sil} = [Na]_{water} \times [SiO_3]_{water}$$

In the case of solution H, we find a slight increase of silica in the silicate compartment and an increase of sodium on the other side of the membrane, which is so far in accordance with the membrane law. Substituting the actual values obtained with parchment membrane, in the above equation we get,

$$[SiO_3]_{sil} = \frac{[Na]_{water} \times [SiO_3]_{water}}{[Na]_{sil}} = \frac{.7748 \times 1.4918}{.766 \times 60.3} = 0.02502.$$

The value experimentally found gives

$$[SiO_3]_{sil} = 0.02499.$$

which is slightly less than the value calculated above. The experimental analytical concentration of silica in the silicate chamber on the contrary should have been slightly higher than the above calculated value because the analytical value represents the sum total of both the non-diffusible silica as well as the ionic silica. Assuming then that the ions in the 2:1 ratio silicate solution are Na^+ and SiO_3^- the above divergence leads one to infer that the non-diffusible aggregate is not only $[(SiO_3)_n]^-$, but consists also of a more complex combination probably containing both sodium and silica.

As the ratio of silica to alkali in the original silicates increases, the distribution across the membranes become more complicated. There is always a larger amount of SiO_3 in the silicate compartment after equilibrium, but there is also a greater amount of sodium in the same compartment. The excess of silica in the silicate compartment, is however proportionately much greater than the excess of sodium in the silicate compartment over the sodium in the water compartment.

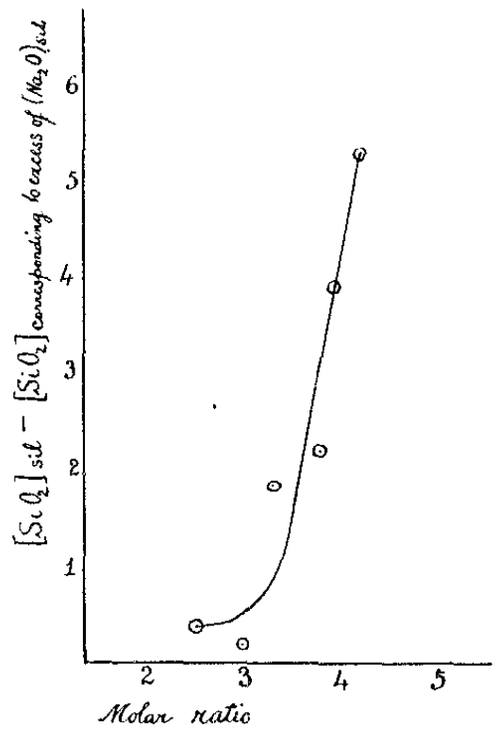


FIG. 2

In the last column of Table III the excess of silica present in the silicate compartments over and above the amounts corresponding to the excess of sodium present, is given.

This amount shows a marked increase at the ratio 3.3. This is clearly seen from Fig. 2, in which the last column of Table III is plotted against the molar ratio of the original silicates. Thus it is evident that the amount of indiffusible silica, whether in the form of complex ions or combined molecules increases at a much enhanced rate after the ratio 3. This result is quite in agreement with the previous observations based on scattering and ultra-microscopic measurements.

The variations of the amounts of non-diffusible matter with change of ratio, are shown more clearly in Tables IV, V.

TABLE III

	Molar ratio	Increase in the silicate compartments		SiO_2 corresponding to Na_2O in the previous column	Difference
		SiO_2	Na_2O		SiO_2
A.	4.2	0.7860	0.0640	0.2612	0.5248
B.	3.95	0.6116	0.0590	0.2240	0.3876
C.	3.8	0.4054	0.0502	0.1855	0.2199
D.	3.3	0.2644	0.0254	0.0815	0.1828
E.	3.0	0.0520	0.0134	0.0391	0.0129
G.	2.5	0.0620	0.0086	0.02334	0.03866

When the equilibrium molar ratios of the two compartments, are plotted against each other, a curve (Fig. 3) is obtained, which shows clearly that the increase in molar ratio in the silicate compartment is far greater than the change in the molar ratio in the water compartment.

TABLE IV
Parchment membrane

	Molar ratio	Equilibrium ratio Silicate Compartment $\frac{[SiO_2]_{sil}}{[Na_2O]_{sil}}$	Equilibrium ratio Water Compartment $\frac{[SiO_2]_{water}}{[Na_2O]_{water}}$	Equilibrium ratio $\frac{[SiO_2]_{sil}}{[SiO_2]_{water}}$	Equilibrium ratio $\frac{[Na_2O]_{sil}}{[Na_2O]_{water}}$
A.	4.2	4.875	3.397	1.7098	1.1916
B.	3.95	4.373	3.356	1.5136	1.1617
C.	3.8	4.056	3.496	1.3132	1.1319
D.	3.3	3.492	3.089	1.1930	1.0558
E.	3.0	3.0208	2.976	1.035	1.020
G.	2.5	2.5345	2.470	1.042	1.0150
H.	2.0	2.023	1.979	1.0105	0.988

TABLE V
Collodion membrane

	Molar ratio	Equilibrium ratio Silicate compartment $\frac{[SiO_2]_{sil}}{[Na_2O]_{sil}}$	Equilibrium ratio Water compartment $\frac{[SiO_2]_{water}}{[Na_2O]_{water}}$	Equilibrium ratio $\frac{[SiO_2]_{sil}}{[SiO_2]_{water}}$	Equilibrium ratio $\frac{[Na_2O]_{sil}}{[Na_2O]_{water}}$
A.	4.2	5.532	2.512	2.797	1.27
B.	3.95	4.960	2.7105	2.274	1.242
C.	3.8	4.257	3.238	1.610	1.224
D.	3.3	3.580	2.974	1.3960	1.160
E.	3.0	3.013	2.986	1.055	1.050
G.	2.5	2.5014	2.493	1.054	1.050
H.	2.0	2.020	1.978	1.009	0.980

When the values in the various columns of the above tables are plotted, curves are obtained, which all show the characteristic change between the points corresponding to 3.0 and 3.3 ratios in the original silicate solutions. The general nature of the curves obtained with both parchment and collodion membranes, is the same. Both sets of curves show practically the same change after the ratio 3.0. In the case of the collodion membrane however there is a greater separation, inasmuch as, the excess of silica concentration in the silicate compartment is proportionately greater than that in the case of the parchment membrane. A possible reason for this might be that the parchment allows certain ions or ionic complexes to pass through, which however are not able to diffuse across the collodion membrane.

The simultaneous presence of an excess of both SiO_2 and Na_2O, in the silicate compartments, shows that a part of the non-diffusible portion must consist of both sodium and silica. There are probably two kinds of non-diffusible matter present in the silicates,

(1). Complex silicate ions like $[(SiO_3)_n]^-$

(2). Complex molecules containing both silica and sodium, which may be represented as

$$[(Na)_x\ (SiO_n)_y]_p$$

The equilibrium state of such a system would thus be as follows,

Silicate compartment	Water compartment
Na^+	Na^+
$(SiO_3)^-$	$(SiO_3)^-$
$[(SiO_3)]_n^-$	Na^+
$[(Na)_x\ (SiO_n)_y]_p^-$	Na^+

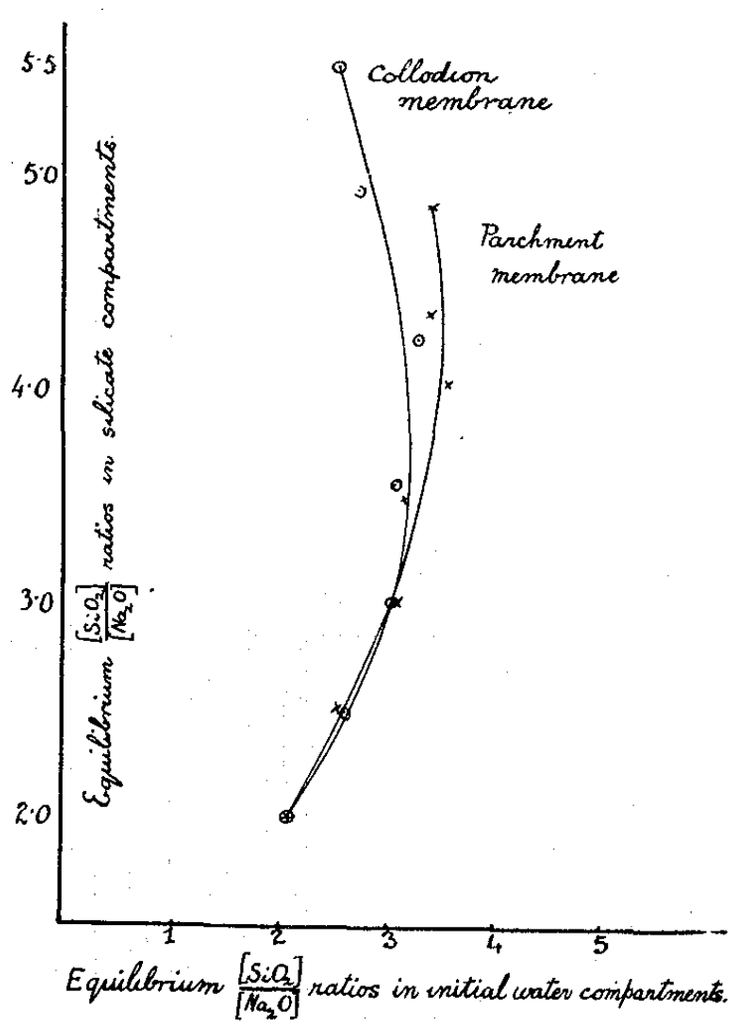


FIG. 3

The molar complex $[(Na)_x\ (SiO_n)_y]_p$, if present in sufficiently large quantity will give at equilibrium a greater analytical value for both SiO_2 and Na_2O in the silicate compartment.

From an examination of Fig. 4, in which the ratio of the sodium contents of silicate and water compartments respectively, have been plotted against the molar ratio of the silicate solutions, it is evident that the sodium silica molecular complexes present in the silicates, increase with increase of molar ratio of the original silicate solutions. This curve also exhibits the characteristic bend after the ratio 3.0, though not so marked as in the other cases.

After the silicate solutions attained equilibrium, they were also used for a series of osmotic pressure measurements. The osmotic pressure of the liquid in the silicate compartment was measured against the liquid in the water compartment. The type of osmometer used is shown in Fig. 5. The results obtained are shown in Table VI.

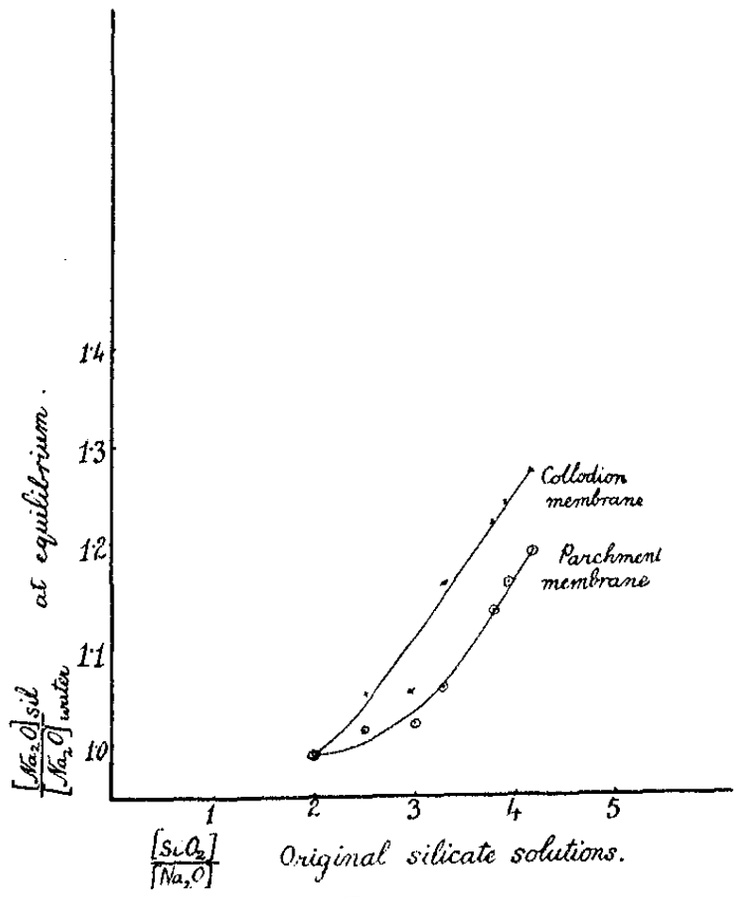


FIG. 4

TABLE VI

Parchment membrane solutions

Molar ratio	Observed osmotic pressures in mm of Hg.	C. where, $C = \frac{M \times p \times T_o}{22.4 \times 760 \times T_1}$
A.	4.2	$10.28 \cdot M \times 10^{-5}$
B.	3.95	$7.8 \cdot M \times 10^{-5}$
D.	3.3	$2.75 \cdot M \times 10^{-5}$
E.	3.0	$1.67 \cdot M \times 10^{-5}$
G.	2.5	$1.55 \cdot M \times 10^{-5}$
H.	2.0	$1.23 \cdot M \times 10^{-5}$

In the last column of Table VI, the percentage of colloidal matter present has been calculated in terms of M, the answer molecular weight of the colloidal material, by using the equation,

$$C = \frac{M\, p\, T_o}{22.4 \times 760 \times T_1},$$

where p is the observed osmotic pressure in mm of Hg, and C is the percentage of colloid.

In Table VI we find that the value of C rises in a very marked way with the rise of ratio of the silicates. By plotting C, the colloid concentration against molar ratios, a curve, Fig. 6, is obtained which shows the same rapid rise after the ratio 3.0.

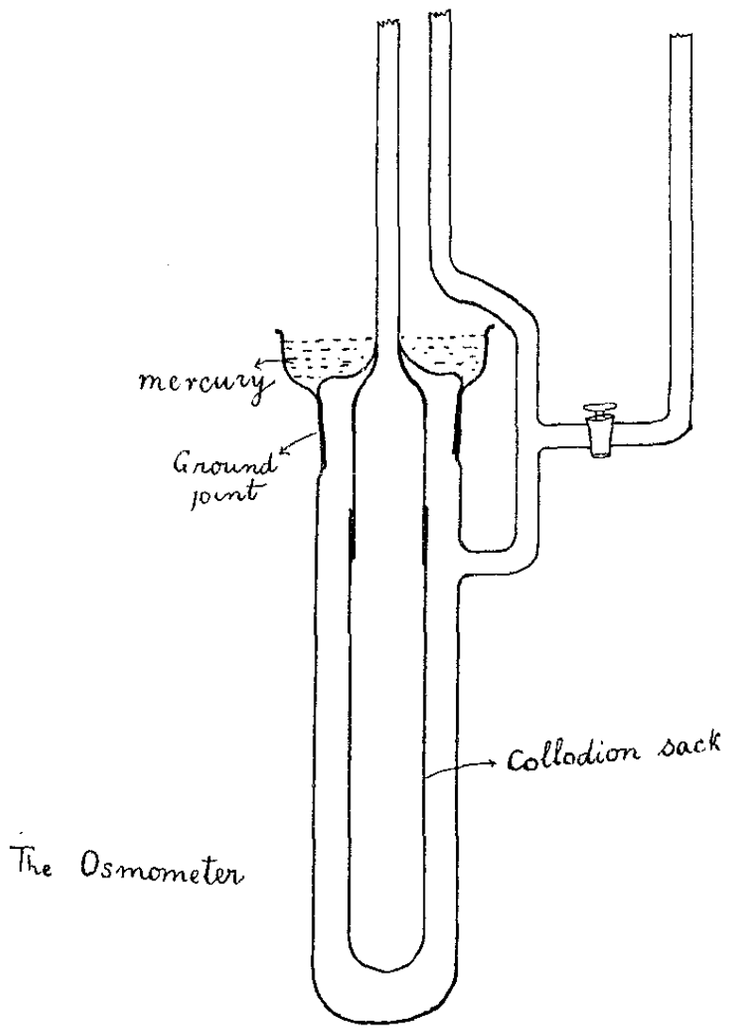


FIG. 5

It is not possible to get any actual measurements of the total colloidal matter present, as nothing is known about M, the average molecular weight of the colloid. So far as these experiments go, they support the general conclusions already arrived at about the constitution of the silicates in relation to increasing ratios of SiO_2 to Na_2O.

Hydrolysis does not seem to play any important role during these distribution processes across membranes. To ascertain this point a few pH measurements of the solutions after equilibrium were done. The pH measurements were done potentiometrically, a hydrogen electrode vessel of the Walpole type being used. A saturated solution of potassium chloride was used as the liquid junction. Some of the results obtained are given in Table VII.

TABLE VII

Hydrolyses in sodium silicate solutions

Solution	Molar ratio	Observed E. M. F. Silicate compartment (volts)	Observed E. M. F. Water compartment (volts)	pH Silicate compartment	pH Water compartment
A.	4.2	0.8930	0.8896	10.88	10.83
C.	3.8	0.8892	0.8862	10.80	10.765
G.	2.5	0.8980	0.8964	10.964	10.937

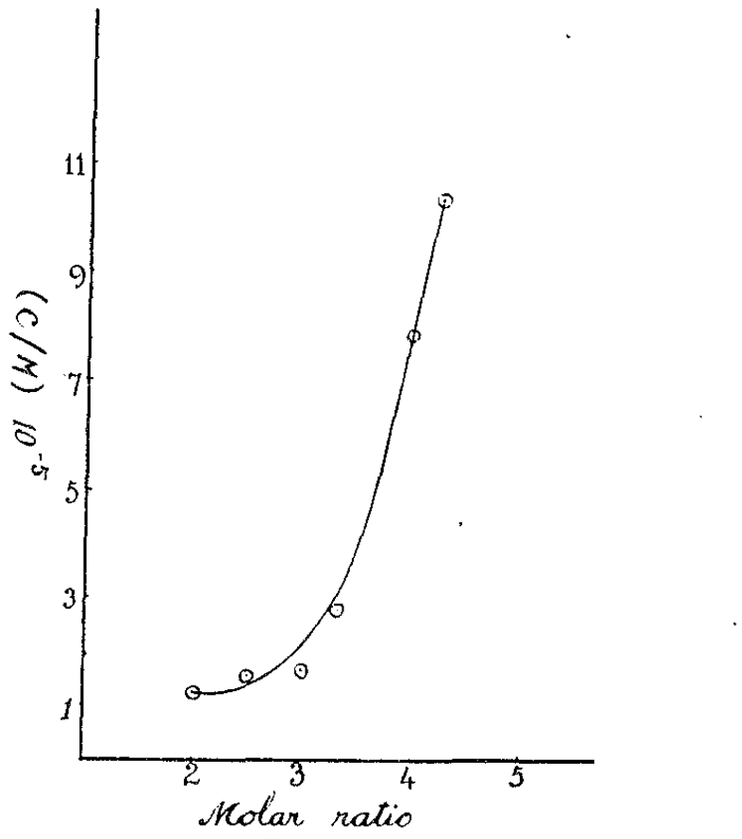


FIG. 6

Considering therefore that [H] × [OH] = K_w, the dissociation constant of water, from the above pH values we find that the solutions in both the compartments, are practically equally hydrolysed. This conclusion is borne out by the experiments of Harman (private communication) who also found that in the higher ratios the silicates were considerably less hydrolysed.

Summary

1. The diffusion across membranes of aqueous sodium silicate solutions, using both parchment and collodion membranes, has been investigated.

2. After equilibrium the solutions have been analysed, and it was found that the silica concentration in the original silicate compartment, was generally greater than the silica concentration in the other compartment.

3. The distribution was greatly dependent on the original molar ratios of the solutions. Solutions up to the molar ratio 3.0, showed very little variations in concentrations during diffusion, showing thereby that the quantity of non-diffusible matter in those solutions, was comparatively small.

4. The quantity of non-diffusible matters increased very rapidly after the ratio 3.0. This result is quite in line with the previous measurements on the light-scattering of the silicate solutions, and shows beyond doubt that after the ratio 3.0, the quantities of colloidal matters in the silicate solutions increases at a very rapid rate.

5. There was generally more silica left in the silicate compartments, but the amount of sodium in the silicate compartments, was also found to be greater than the amount of sodium in the water compartment. This is interpreted to indicate that the colloidal matters present in the higher ratio silicate solutions, are in the form of molecular aggregates or ionic complexes containing both sodium and silica. It is suggested that the equilibrium state is as follows:

Silicate compartment	Water compartment
Na^+	Na^+
$(SiO_3)^-$	SiO_3^-
$[(SiO_3)_n]$	Na^+
$[(Na)_x\ (SiO_n)_y]_p$	Na^+

6. A series of osmotic pressure measurements of the solutions after equilibrium, showed that the quantity of colloidal matters in the silicates increased with ratio.

7. Measurements of pH of the solutions after equilibrium showed that hydrolysis does not take any prominent part during these distribution processes.

In conclusion the author wishes to express his thanks to Prof. F. G. Donnan, for his many valuable suggestions and for his kind interest in this work.

The William Ramsay Laboratories Physical and Inorganic Chemistry,
University College, London

THE METHANE EQUILIBRIUM IV

BY R. C. CANTELO

The data given in the third paper[1] of this series permits the calculation of the free energy decrease attending the synthesis of *methane from amorphous* carbon and hydrogen.

The free energy expression for the Second Law of Thermodynamics is given by

$$d\left(\frac{-\Delta F}{T}\right) = \frac{\Delta H}{T^2} \cdot dT \text{ and } \Delta H,$$

the increase in heat content may be expressed in terms of the heat capacities of the substances involved.

If ΔC represents the difference in the heat capacities of the products and the reactants, the equation becomes

$$-\frac{\Delta F}{T} = \int \frac{\int \Delta c \, . \, dT + \Delta H_o}{T^2} \cdot dT + I$$

where ΔH_o and I are constants of integration.

ΔH_o *may be calculated from the fact that for the reaction*

C (amorph) $+ 2H_2 \rightleftarrows CH_4$; $-\Delta H_{293} = 21{,}730$ calories

If ΔC be expressed in series form,

$\Delta C = \Delta C_o + \alpha T + \beta T^2 + - - -$

and the free energy expression simplifies to

$$\frac{-\Delta F}{T} = \frac{-\Delta H^\circ}{T} + \Delta C_o \ln T + \frac{\alpha}{2} T + \frac{\beta}{6} T^2 + I$$

or

$$-\Delta F = -\Delta H_o + \Delta C_o \, T \ln T + \frac{\alpha}{2} T^2 + \frac{\beta}{6} T^3 + I \, T$$

Dixon, Campbell, and Parker[2] determined the C_p^T/T curve for methane and gave the linear equation

$$C_p^T = 3.47 + 0.019 \, T$$

to represent their results. This equation is used in the calculations given below.

For hydrogen[3]

$$C_p^{0.T} = 6.52 + 0.00044 \, T.$$

For carbon[4]

$$C_p^{0.T} = 1.1 + 0.0024 \, T + 4.0 \, . \, 10^{-7} T^2$$

This latter equation gives the value 2.4 for the atomic heat of carbon at ordinary temperatures. The atomic heat of amorphous carbon at ordinary temperatures is 2.6.

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[1] J. Phys. Chem., **31**, 246 (1927)

[2] Proc. Roy. Soc., **100A**, 1 (1921).

[3] Saunders: J. Phys. Chem., **28**, 1151 (1924).

[4] Lewis and Randall: "Thermodynamics and Free Energy," 569 (1923).

These values give

$$\Delta C_o = -10.67$$
$$\alpha = +0\ 01572$$
$$\beta = +4.0 \cdot 10^{-7}$$

The free energy equation thus becomes

$-\Delta F = 19{,}280 - 10.67\ T \ln T + 0.000786\ T^2 + 0.6 \cdot 10^{-7} T^3 + I\ T.$

The value of I, the constant of integration, may be determined from the values of $-\Delta F$ calculated from the determined equilibrium constants. For this calculation, the values obtained by the writer with ethylene as the initial system were used. This gave an average value of 42.2. The "constant" varied between +41.3 and +43.3.

$-\Delta F = 19{,}280 - 10.67\ T \ln T + 0.0786\ T^2 + 0.0000006 T^3 + 42.2\ T$

which gives for T = 298 that

$-\Delta F_{298} = 14{,}500$ calories for the reaction C (amorph) + $2H_2 \rightleftarrows CH_4$.

Lewis and Randall[1] have calculated $-\Delta F_{298}$ for the reaction

C (graph) + $2H_2 \rightleftarrows CH_4$; $-\Delta F_{298} = 12{,}800$ calories and C (amorph) + $2H_2 \rightleftarrows CH_4$; $-\Delta F_{298} = 14{,}500$ calories from which for the reaction

C (amorph) $\longrightarrow$ C (graph); $-\Delta F_{298} = 1{,}700$ calories.

Summary

The free energy decrease attending the synthesis of methane from amorphous carbon and hydrogen has been calculated and found to equal 14,500 calories.

Department of Chemistry,
University of Cincinnati,
Cincinnati, Ohio.

[1] "Thermodynamics and Free Energy," 572 (1923).

ADSORPTION BY METALLIC HYDROXIDES. I ADSORPTION OF ARSENIOUS ACID BY PRECIPITATED FERRIC HYDROXIDE

BY KSHITISH CHANDRA SEN

General Introduction

The study of adsorption of various substances by means of hydrated oxides as adsorbents has been done mainly from two points of view, namely (1) to compare their adsorptive power with adsorbents such as animal charcoal, etc, and (2) whether any relation between the coagulating power and adsorption of ions exists or not. In the first case, mainly the adsorption of dyes and in some cases that of acids and salts has been examined whereas in the second case both salts and acids were used with a colloidal solution of the hydroxide. As an instance of the first case, a paper by Freundlich and Poser,[1] in which a comparative study of the adsorptive power of alumina, bole and animal charcoal on some basic and acid dyes, and of salts of the alkaloids and certain other organic bases was made, may be mentioned. The papers by Gann,[2] Ishizaka,[3] and those by Weiser and his collaborators,[4] are examples of the second type. There is another investigation which has drawn the attention of several investigators, namely the adsorption of arsenious acid by hydrated ferric oxide. Besides these—though stray cases of adsorption by hydrated iron, aluminium and chromium oxides appear in the literature, it seems that no systematic attempt has been made to make a comparative study of the adsorptive power of these hydroxides for inorganic and organic acids.

In a previous paper,[5] I have shown that when a ferric chloride solution is mixed with sufficient quantity of arsenious acid, and then caustic alkali is added, no precipitation of the ferric hydroxide occurs, but instead a colloidal solution of negatively charged ferric hydroxide is obtained. In a later paper,[6] the same behaviour with chromium hydroxide was also shown. These results indicated that the stabilisation of the hydroxides may be due to the adsorption of the negatively charged arsenite ions, and hence about two years ago an investigation on the adsorptive power of these hydroxides for arsenious acid was started. The results obtained were of sufficient interest to extend the investigation to other acids, mainly organic, the experiments being done with all the three oxides under varying conditions. The object of this series of papers is to present the results obtained, and their possible application to the theoretical problems of adsorption and colloid coagulation has been pointed out.

[1] Kolloidchem. Beihefte, 6, 297-328 (1914).
[2] Kolloidchem. Beihefte, 8, 63 (1916).
[3] Z. physik Chem., 83, 97 (1913).
[4] J. Phys. Chem., 24, 30, 630 (1920).
[5] J. Phys. Chem., 28, 313 (1924).
[6] Kolloid-Z., 34, 262 (1924).

Adsorption of Arsenious Acid by Ferric Hydroxide

The adsorption of arsenious acid by ferric hydroxide has been studied by several authors. The investigation was started by Bunsen and Berthold,[1] who observed the great adsorption power of ferric hydroxide for arsenious acid and considered the combination to be a basic ferric arsenite. Seventy years after the publication of this result, the subject was quantitatively investigated by Biltz[2] who concluded that it was a case of adsorption and not chemical combination, since it follows the so-called adsorption law expressed by a equation of the type $(x/m)^n = kC$, where x/m is the amount of the solute taken up per gram of the adsorbent, C is the concentration in the solution at equilibrium and n and k are constants. In his experiments Biltz found that the values of n and k were respectively 5 and 0.631. In later years, Lockemann and Paucke,[3] and Lockemann and Lucius[4] studied the conditions under which the adsorption of arsenious acid from solution is complete. The results obtained by the latter authors show that a given amount of arsenious acid is removed from solution by a considerably smaller amount of precipitate when an exactly stoichiometric amount of ammonia is used than when twice that amount is used. They also observed that the adsorption of arsenious acid is considerably reduced by the use of potassium hydroxide or sodium hydroxide instead of ammonia. Mecklenburg[5] worked with ferric hydroxide and arsenious acid in demonstrating his principle of "affine Adsorptionskurven" i. e. adsorption curves, so related, each by a particular factor, to an unit curve, that the ordinate corresponding to any given abscissa on one of the curves may be obtained by multiplying, by the factor, the ordinate on the unit curve corresponding to the given abscissa. He showed that the adsorption curves obtained from differently prepared samples of hydrated ferric oxide were actually related in such a way to an unit curve, which he at first determined for one particular preparation. In a recent paper Boswell and Dickson[6] have again studied the subject and have come to several interesting conclusions. They used a two-month old sample of precipitated ferric hydroxide and they did not find any ageing effect of the hydroxide on its adsorption power. The adsorption of arsenious acid was found to be diminished by the presence of sodium hydroxide, but the adsorption of sodium hydroxide was found to be increased by the presence of arsenious acid. In supporting further the generalisation of Mecklenburg to the effect that where the adsorption of a compound from solution follows the equation of the type $E = \beta A^p$, p is a constant for the same adsorbing material, and that an adsorbent prepared under various conditions, or of various ages will vary only in the value of β, Boswell and Dickson have shown that p remains constant for different preparations of ferric hydroxide where arsenious oxide alone was used. In Table I the results calculated for various preparations are shown.

[1] "Das Eisenhydroxyd," (1834).
[2] Ber., **37**, 3138, (1904).
[3] Kolloid-Z., **8**, 273 (1911).
[4] Z. physik. Chem., **83**, 735 (1913).
[5] Z. physik. Chem., **83**, 609 (1913).
[6] J. Am. Chem. Soc., **40**, 1793 (1918).

TABLE I

Constants for the equation $E = \beta A^p$ for ferric hydroxide

Series	Precipitation temperature	p	β
Boswell and Dickson			
(1) pure As_2O_3		0.210	128
(2) As_2O_3—constant NaOH		0.284	333
Mecklenburg	1°	0.183	195
Do	11°-12°	0.188	184
Do	23°	0.197	184
Do	45°	0.186	180
Do	51°	0.195	170
Do	60°	0.187	170
Do	98°	0.195	120
Do unit curve	—	0.188	200
Do air-dried	98°	0.195	43
Biltz	—	0.198	170

These results support the conclusions of Mecklenburg to a certain extent. As the results obtained by me are somewhat different, an account now will be given of the effect of ageing, different method of preparation, etc., on the adsorptive power of ferric hydroxide under different conditions.

Experimental method.

The ferric hydroxide was always precipitated at the room temperature (about 25°C), from a 2 N solution of $FeCl_3$ with excess of dilute ammonia, care being taken to avoid any rise in the temperature by immersing the whole vessel in cold water. The precipitate was usually highly gelatinous, and it was washed partly by decantation and finally by dialysis till completely free from chloride. The freshly precipitated substance was dark brown, but when one sample was allowed to "age" under water, after four months it became dull red. All the samples were kept always covered with water. In making the adsorption experiments, 10 cc of this hydroxide was taken out by means of a pipette, and introduced into a 100 cc flask. The necessary amount of the solute was then poured into the flask, and water was added up to the mark. The whole thing was shaken several times at constant intervals and then allowed to settle for a fixed time. The supernatant liquid was then analysed iodometrically in presence of sodium bi-carbonate. Many observations showed that there was no appreciable error in taking out the ferric hydroxide by means of the pipette, the maximum being 0.2 per cent. In course of the investigation, it was found advisable to use a constant quantity of some neutral salt like KCl in the flasks, otherwise a peptisation of the hydroxide took place, and the supernatant liquid became turbid. It was however found out that the presence of this salt exerted no effect on the amount of adsorption by hydrated ferric oxide. In some preliminary cases, ammonium chloride has been used as the salt. Where acids or alkali have been used as the

solute, they were titrated by means of carbonate free alkali or standard acid with phenolphthalein as the indicator. The time of settling was usually 20 hours and the volume 100 cc.

From preliminary experiments it was found that the adsorption results were quite reproducible. In Table II the effect of ammonium chloride is shown.

TABLE II

Concentration of As_2O_3 in grms.	Adsorption in grams. No NH_4Cl	$NH_4Cl = .013$ mole litre	$NH_4Cl = .02$ mole litre.
0.1578	———	0.09228	0.09228
0.12624	0.08748	———	0.08748
0.09468	0.07448	0.07448	0.07448
0.06312	0.06236	0.06236	0.06236

These results show that the addition of ammonium chloride has no effect on the final equilibrium and potassium chloride also behaves similarly. At this place, some experiments were made to test the reversibility of the equilibrium between arsenious acid and ferric hydroxide. Biltz (loc. cit.) has already shown that the equilibrium is reversible and my experiments have also supported it. It will be shown later on that the effect of time on this adsorption is also nil when three hours are allowed for the adsorbent to settle down. In the following table the effect of concentration of the arsenious acid on its adsorption by a fixed amount of ferric hydroxide is shown. The hydroxide is the same as used in the previous experiments.

TABLE III

Adsorption of arsenious acid

wt. of Fe_2O_3 = 0.2645 grms.

Original concentration As_2O_3 in grms	Concentration after adsorption	Adsorption in grms by 1 gr. adsorbent
0.4901	0.3661	0.4688
0.4593	0.3363	0.4650
0.3977	0.2793	0.4477
0.3367	0.2223	0.4325
0.2840	0.1967	0.4057
0.25248	0.14968	0.3890
0.2209	0.1193	0.3841
0.18936	0.0909	0.3723
0.1578	0.08552	0.3469
0.12624	0.03876	0.3308
0.09468	0.02020	0.2816
0.06312	0.00076	0.2356

The hydroxide used in the above investigation was prepared only a few days before the actual experiment was made. Its colour was dark brown, and this sample was now put inside a stoppered bottle and kept in a dark place for four months in order to investigate the effect of ageing. The temperature

of the outer atmosphere rose about 6° higher during this interval. On opening the vessel after about four months, it was found that the colour of the sample was now dull red, and though the hydroxide was always kept under water, it appeared to have been dehydrated and agglomerated. Though this is curious, it seems to be the only explanation of this remarkable colour change.[1] The weight of ten cubic centimeters of the substance as withdrawn by the pipette remained constant, and in Table IV are the results obtained by using this sample as the adsorbent of arsenious acid is given. Other conditions remain the same:

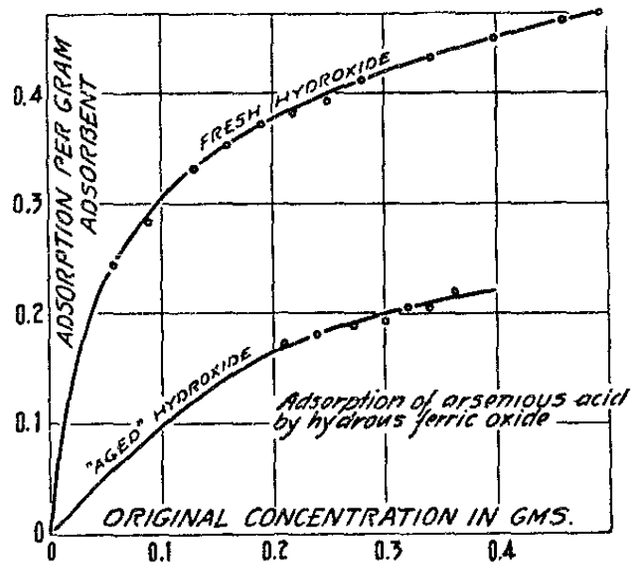


FIG. 1

TABLE IV

Original conc. of As_2O_3 in grms.	Conc. after adsorption	Adsorption in gms. by 1 gr. of the adsorbent
0.3638	0.30584	0.2192
0.34178	0.28865	0.2008
0.31947	0.26680	0.1992
0.29739	0.24610	0.1939
.0.27508	0.22770	0.1792
0.2369	0.19021	0.1765
0.20861	0.16215	0.1757

The results given in Tables III and IV are plotted in Fig. 1. It will be obvious that the ageing has an appreciable effect on the adsorptive power of ferric hydroxide and that the actual amount of adsorption greatly decreases due to this ageing effect. It has already been mentioned that Boswell and Dickson did not find any ageing effect on their ferric hydroxide. My results are therefore different from theirs and it became a matter of interest to investigate this subject further. It has been found that this ageing effect is quite appreciable after the first few days of the preparation of the oxide, but

[1] Weiser: J. Phys. Chem., 24, 286 (1920).

after about 25 days, the effect of ageing is not appreciable. This means that the hydroxide changes at first rather quickly, but after sometime this change is very slow. In the light of these experiments, the result of Boswell and Dickson becomes apparent, for these investigators used a two-month old hydroxide for adsorption experiments. In Table V, the adsorptive power of the fresh hydroxide is compared to that of the aged hydroxide when the original concentration of the arsenious acid is the same. The values have been obtained from the experimental curves.

TABLE V

Original conc. or As_2O_3 in grms.	Fresh hydroxide	Amount adsorbed by one gram of the aged hydroxide
0.10	0.300	0.0967
0.15	0.347	0.180
0.20	0.373	0.160
0.25	0.397	0.180
0.30	0.417	0.197
0.40	0.447	0.280

It will thus be observed that the amount of adsorption by an old sample of ferric hydroxide is about fifty per cent less than that of the fresh one.

Effect of time.

In all the results given above, the time allowed for the equilibrium to set in has been 20 hours. At this point it became desirable to investigate the effect of time, if any, on the equilibrium concentrations. Many experiments were made which showed that if the hydroxide particles are allowed to settle completely, the final concentration of the solute in the supernatant liquid is always the same. In Table VI is the result obtained with the aged sample.

TABLE VI

Original conc. of As_2O_3 in grm.	Amount adsorbed per gram adsorbent	
	Time 3 hours	Time 20 hours
0.2369	0.1765	0.1765

This result shows that the equilibrium was reached within three hours, and the adsorption does not change with the increase in the duration of the contact of the solute with the adsorbent.

Experiments with different samples

In the experimental results already recorded, the same material under two different conditions has been examined. It was now thought desirable to investigate whether Mecklenburg's generalisation as to the constancy of the value of the exponential factor in the adsorption equation is true for our samples or not. For this experiment, two other samples of ferric hydroxide were prepared, the method of preparation being almost the same as before. For the sake of convenience the hydroxide already examined will be denoted as sample No. 1, whilst the aged one will be denoted as No. 1a. In Table VII the results obtained with the sample No. 2 are shown.

TABLE VII

Fe_2O_3 = 0.4719 gr.
NH_4Cl = .02 mole per litre
Vol. = 100 cc. Time 20 hours.

Original conc. in grms.	Conc. of the solution after adsorption	Amount adsorbed by 1 grm. adsorbent.
0.7713	0.6365	0.2856
0.7230	0.5896	0.2828
0.6748	0.4429	0.2796
0.4820	0.3522	0.2751
0.4338	0.3051	0.2728
0.3856	0.2621	0.2617
0.3374	0.2176	0.2541

In Table VIII, the results with sample No. 3 is shown. In this experiment, ammonium chloride was replaced by potassium chloride, the concentration of which was 0.05 mole per litre. Potassium chloride however had no effect on the equilibrium between the hydroxide and the arsenious acid. The amount of Fe_2O_3 used was 0.2539 gr. The other conditions remain the same.

TABLE VIII

Original conc. of As_2O_3 grms.	*Conc. of the solution* after adsorption	*Amount adsorbed* by 1 grm. adsorbent
0.2892	0.2270	0.2431
0.2410	0.1802	0.2376
0.1928	0.1334	0.2322
0.1446	0.0877	0.2224
0.0984	0.0456	0.1986

In Table IX the results obtained by varying the amount of adsorbent No. 3 have been recorded. The original concentration of the arsenious acid 0.2892 gr. was the same in all cases, the amount of ferric hydroxide actually taken being in each case different. It is interesting to note the change in the actual amount of adsorption calculated per gram of the adsorbent with the change in the amount of the adsorbent taken for experiment. This result is shown in Fig. 2 as No. 3a.

TABLE IX

Amount of adsorbent in grms.	Conc of the solution after adsorption	Amount adsorbed by 1 grm. adsorbent.
——	0.2892	——
0.2559	0.2270	0.2431
0.5118	0.1661	0.2405
0.7677	0.1123	0.2304
1.0236	0.0714	0.2127

In order to make a comparison in the values of the exponential factor of the several samples, the logarithmic curves have been drawn and are given in Fig. 2. Only the simple equation $(x/m)^n = kC$ has been used where x/m is the amount of the solute adsorbed per gram adsorbent and C the concentration of the solution in grms. at equilibrium, n being the exponential constant,

and k the other constant. The abscissa and the ordinate represent the values of log x/m and log C respectively, and the values of n have been obtained from the curve, n being the slope of the curve.

It will be seen from Fig. 2, that the logarithmic curves all approximate to straight lines showing thereby that the adsorption equation is applicable in these cases. The values of the constant are shown in Table X. It may be pointed out that in our form of the equation, the value of n is the reciprocal of that used in the form in Mecklenburg's paper.

TABLE X

Sample of hydroxide	n	1/n
No. 1	5.67	.176
No. 1a	4.51	.221
No. 2	9.51	.105
No. 3	11.43	.087
No. 3a	11.43	.087

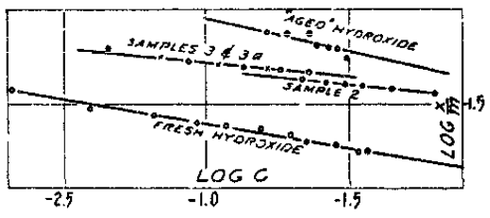


FIG. 2

These results reveal two interesting facts. The first is that the exponential n remains only approximately constant when a fresh and an aged sample of the same preparation are used, the difference in the values of k being great. When however different preparations are used, the value of n varies appreciably. This will be evident when the values of n for samples 1, 2 and 3 are compared. It will also be interesting to note the values of $1/n$ given in Table X and the values of p given in Table I. The difference is so marked that it appears that the conclusion of Mecklenburg is limited in its application. Another interesting fact observed in this connection is that if experiments are made with the same adsorbing material but under different conditions which however do not affect the adsorbent in any way, then the values of both the constants in the adsorption equation remain the same. This will be seen from the curves where results with No. 3 and No. 3a are represented by the same straight lines.[1]

It has already been stated that both Lockemann and Lucius (loc. cit.) and Boswell and Dickson have found that the presence of caustic alkali decreases the adsorption of arsenious acid considerably. The latter authors further found that though the amount of adsorption of arsenious acid is decreased in presence of caustic alkali, the adsorption of the latter however is increased in the presence of arsenious acid. In view of this curious result some experiments were carried out to determine the adsorption of pure sodium arsenite and sodium hydroxide separately at the same concentration. The sodium arsenite was estimated iodometrically by means of iodine solution in presence of sodium hydrogen carbonate, and the alkali was estimated by means of

[1] Some recent experiments with manganese dioxide show that even this is not true in the case of adsorption of some salts like copper sulphate.

standard hydrochloric acid with phenolphthalein as the indicator. In order to make a comparative study, the adsorption of pure arsenious acid was also investigated side by side with that of sodium arsenite. In the following tables, the results obtained are given. As there was some doubt as to whether simply the arsenite ion or the sodium arsenite as a whole is adsorbed, the values are expressed in terms of iodine. Ammonium chloride was added in the experiments with the arsenite, but no ammonium salt was added when the adsorption of the alkali was determined.

TABLE XI

Sample No. 1a—0.2645 gr.

Original conc. of arsenite in terms of I_2 milli-equivalents per 100 cc.	Amount of adsorption in terms of I_2
9.320	1.152
7.767	1.133
6.215	1.067
4.660	1.002

TABLE XII

Adsorption of NaOH of approximately same strength as sodium arsenite.

Same sample of Fe_2O_3

Original conc. in milli-equivalents	Adsorption in milli-equivalents
9.210	0.2351
7.676	0.2250
6.141	0.2150
4.606	0.2050

TABLE XIII

Sample 2—0.4719 gr.

Original conc. of arsenite in terms of I_2—milli equivalents	Adsorption in terms of iodine
9.320	2.757
7.767	2.715
6.215	2.673
4.660	2.583

The results given above show that sodium arsenite is highly adsorbed by ferric hydroxide, and the adsorption of alkali is also appreciable. When however a comparison was made between the adsorption values of arsenite and arsenious acid, an apparently anomalous result was obtained. It was found that with the sample of ferric hydroxide No. 1a, with dilute arsenite the adsorption is greater than that of pure arsenious acid of the same concentrations in terms of iodine. With higher arsenite concentration however, the adsorption value becomes less than that of pure arsenious acid. With sample No. 2, the adsorption of arsenite was always higher than that of pure arsenious acid in the concentration studied. Since sodium arsenite hydrolyses to a great extent in water, it is probably that when sodium arsenite is used as the solute, actually the simultaneous adsorption of alkali and arsenious acid by hydrated ferric oxide is observed. Hence when alkali is present, the adsorp-

tion of arsenious acid should in general decrease owing to the simultaneous adsorption of the alkali. As a matter of fact this has been observed by a number of investigators already cited. It is rather difficult to explain however the contradictory results already recorded, and further experiments are being done to arrive at a satisfactory conclusion.[1]

In the foregoing pages, I have discussed the effect of ageing, different method of preparation of the adsorbent, the effect of neutral salts, the effect of change in the concentration of the solute, and the effect of varying the amount of the same adsorbent, on the amount of adsorption of arsenious acid. All these experiments were however done at a constant volume of 100 cc. In the following tables, some more results dealing with the effect of volume of the solution on adsorption are given. In these experiments, ferric hydroxide sample No. 3 has been used, the weight of the adsorbent being 0.2559 gr. and potassium chloride has been used instead of ammonium chloride.

Effect of volume when the normality of the acids is constant. The actual amount of solute is thus different.

TABLE XIV

Adsorption of As_2O_3. Concentration = 0.1928 gr. per 100 cc

Volume	Amount adsorbed in gms.
10 cc	.05943
50 cc	.05604

TABLE XV

Adsorption of sulphuric acid. Concentration = 0.5491 milli-equivalent per 100 cc.

Volume	Adsorption in milli-equivalents
100 cc	0.3792
50 cc	0.2456

TABLE XVI

Adsorption of benzoic acid Concentration = 0.7358 milli-equivalents per 100 cc.

Volume	Adsorption in milli-equivalents.
100 cc	0.3301
50 cc	0.2736

Effect of volume when the total solute is same. The strength in terms of normality is thus different.

TABLE XVII

Adsorption of As_2O_3 Concentration = 0.0964 gr.

Volume	Amount adsorbed in grms.
100 cc	0.05077
50 cc	0.056628

[1] New experiments show that this behaviour is shown by other samples of hydroxide also when Merck's sodium arsenite is used. By working with sodium arsenite prepared by mixing caustic soda with arsenious acid, the results of Boswell and Dickson have been confirmed.

TABLE XVIII

Adsorption of benzoic acid. Concentration = 0.3679 milliequivalents.

Volume	Adsorption in milli-equivalents.
100 cc	0.2641
50 cc	0.2736

These results emphasise the importance of the volume of the solution in which adsorption is studied. It will be observed that when the total solute is constant, the less the volume, the greater is the adsorption. Whilst with the same normality of the solution but different absolute amount of the solute, the amount of adsorption increases with the volume of the solution. In other words it becomes proportional to the quantity of the solute.

Having thus studied the adsorptive power of hydrated ferric oxide under various change of conditions, a systematic study of the adsorption of different mineral and organic acids was made. Since in these preliminary researches it was observed that the amount and the nature of the hydrated ferric oxide exert a considerable effect on its adsorptive capacity, it was necessary to use the same amount of ferric hydroxide of the same preparation in a constant volume of the solution for a comparative study. For this reason, the ferric hydrogen sample No. 3 has been used in all the experiments to be given in the next paper.

Chemical Laboratory,
Allahabad University

CELL MITOSIS

BY WILDER D. BANCROFT AND CHARLES GURCHOT

Some years ago, our attention was called by Professor Chambers and Mr. I. H. Page of the Cornell Medical College to the fact that the physical chemistry of cell division was in a rather confused state, and we were asked to give our opinion as to the general theory. All the experiments were done by Mr. Gurchot.

The general problem can be stated in a very simple manner. If we have a drop of liquid and if we lower the surface tension locally at two opposite poles, will the drop constrict and tend to break into two drops at the equator where the surface tension is relatively high or along a line passing through the poles, where the surface tension is relatively low?

In 1876 Bütschli stated that such a drop would split along the equator, it being pinched in two by the action of the relatively high surface tension along that line. T. Brailsford Robertson[1] has put forward and defended the opposing view that the drop pulls apart where the surface tension is the lowest. "In a continuous fluid surface of variable tension the regions of high superficial tension must be convex to the outer medium while those of low superficial tension must be concave to the outer medium. If this concavity occurs all round an equatorial circumference a dumb-bell shaped surface will be produced of which the equatorial (approximately cylindrical) portion may be short or long according to whether the slope of the cleft is steep or gradual. If this process (reduction of tension) proceeds sufficiently far to cause the length of the equatorial cylindrical portion to become equal to its circumference, it will break and one drop will split into two."

The flaw in this reasoning is the assumption that an area of relatively high surface tension must be convex to the outside medium. It is true that a drop of one liquid at the bottom of a beaker filled with another liquid will be more nearly spherical, the higher the surface tension. With a lower surface tension the drop will flatten out more under the influence of gravity. The flattened drop is less convex than the spherical one on the top and more convex at the sides—a point which Robertson has overlooked. Robertson then introduces the tacit assumption that a further lowering of the surface tension would cause a greater effect in the same direction and that, having gone from convex to flat on the upper side, it will then go from flat to concave. In the first place, it will not do that. The drop will spread out thinner and thinner, until it forms a layer one, or at most two, molecules thick, after which it will spread no more, so far as we now know. In the second place, this has very little to do with the case in question, because we are not dealing with localized differences of surface tension except in so far as the action of gravity sets up different surface tensions in different parts of the drop.

[1] Archiv Entwicklungsmechanik, **27**, 29 (1909); **32**, 368 (1911); **35**, 692 (1913).

Robertson offered some experiments with olive oil in support of his views. He placed a thread soaked in alkali round a drop of oil submerged in water by addition of chloroform. Since the alkali reacts with the olive oil to form soap, this lowers the surface tension. The drop separates into two drops along the line of the thread, as though it had been cut in two by the thread. At first sight this experiment seems conclusive.

McClendon[1] supports Bütschli's views that a drop of liquid will tend to split into two drops along the line where the surface tension is relatively highest. He considers "that in Robertson's experiment the oil drop is divided by the gravitation of the thread which has been soaked in an alkaline solution. The alkali reduces the surface tension, thus reducing the resistance to division, and thus allows division by a thread of less weight than would otherwise be necessary. This seems to be a just criticism because Robertson[2] admits that "light threads of sewing-cotton cannot be employed with success as they float upon the top of the oil-droplet without sinking into it; the diminution in tension is, consequently, not equatorial. I obtain the best results with linen threads 0.4 mm. in diameter. Linen threads 0.2 mm. in diameter only, float upon the surfaces of the drops and rarely cause division." Robertson accounts for this fact in a different way. He says, when discussing the weight of the thread, that "it is not sufficient that a small sector of an equatorial circumference of the drop be touched by alkali; it is necessary that soap should be formed in the periphery of an equatorial plane. This cannot occur unless the weight of the thread is sufficient to cause it to sink a little way into the drop." It apparently did not occur to Robertson that he could soak the thread in soap instead of in alkali.

McClendon did a set of experiments of his own. "It is not my ambition to imitate cell division exactly with a model; but an analysis of the following experiment may throw some light on what happens when a cell divides. A stender dish is half filled with distilled water and a funnel inserted so that the stem reaches the bottom. A saturated solution of pure sodium chloride in distilled water is poured very slowly into the funnel so that the salt solution comes to lie beneath the pure water without much mixing. About 1 cc. of the chloroform-oil mixture is poured in, so that it forms a drop suspended in the liquid. Two pipettes are filled with fifth-normal sodium chloride solution and quickly introduced into the water, and the alkali allowed to flow gently against opposite poles of the drop. If the alkali reaches both poles at the same time and in the same quantity, the drop elongates along the polar axis and usually constricts into an hour-glass shape. It often divides into two at the constriction. The conditions necessary for complete division are very limited, as is explained in the following analysis of the experiment.

"The alkali reduces the surface tension at the poles and the pressure [?] inside the drop causes a bulging of these regions. At the same time the polar

[1] Am. J. Physiol., **27**, 240 (1910); Archiv Entwicklungsmechanik, **34**, 263 (1912); **37**, 233 (1913).

[2] Archiv Entwicklungsmechanik **35**, 695 (1913)

surface films spread and the equatorial surface film contracts, producing vortex movements in the drop and in the medium. These movements may be demonstrated by mixing a little soot with oil and a few carmine grains with the water. The surface currents carry the alkali toward the equator and enlarge the polar regions of reduced tension. The rapid fall in the internal pressure caused by the rapid enlargement of the surfaces of low tension allows a constriction of the equatorial region. The equatorial surface is not concave (as Robertson intimates) but remains convex until the meridional concaveness equals the equatorial convexness. When the surfaces of reduced tension have expanded until the area of high tension forms but a narrow band around the constricted equator, this band acts like an isolated band of a tension equal to the tension of its surface minus the tension of the surface of the polar regions. The entire force of this residual tension is exerted toward the division of the drop. However, the completion of the division takes time, and the band is reduced rapidly in width by the spreading of the alkaline surfaces. If the constriction is not completed before the alkali spreads over the whole drop, the drop returns to a spherical shape. Therefore it is unusual that a complete division of the drop occurs. Failure to perform this experiment is due to lack of dexterity. The smaller the drop, the (relatively) greater is the dexterity required. Pipettes with capillary openings are more easily controlled, and the concentration of alkali may be increased to compensate for reduced quantity, but it should not be heavier than the salt solution."

Robertson says: "I have repeated this experiment of McClendon's a number of times and under a variety of conditions and I regret to have to admit that I have hitherto been unable to obtain precisely the appearance which he illustrates. Doubtless this is due to some defect in my technique; but, granting this to be the case, the phenomenon described by McClendon is only indirectly due to molecular forces and does not bear upon the mechanics of cell division at all.

"Briefly, what I observe in repeating McClendon's experiment is the following:—as soon as the alkali touches the drop of oil (which is resting upon the flat bottom of a glass vessel), the drop ceases to be spherical and flattens quite suddenly. Transiently, the flattened mass may bulge in irregular shapes towards the pipettes; but the usual effect (if the alkali be not too strong) which immediately succeeds this is a gathering up of one or other or both of the equatorial extremities of the mass into a more or less globular form and an elongation of the mass equatorially in a direction perpendicular to the line joining the openings of the pipettes. If this takes place at both equatorial extremities at once, division of the mass into two may actually occur in a plane perpendicular to the plane of division which is depicted by McClendon.

"It is easy to understand what is really taking place under these circumstances. The forces acting upon a drop which is resting upon a flat surface are not purely molecular; gravity is also acting and tending to flatten the drop and cause flowing in a lateral direction. This tendency is resisted by the surface tension of the drop; but, if the superficial tension be reduced over any

considerable area, bulging will occur and the fluid will flow towards the side of reduced tension because the centre of gravity of the fluid mass is lowered thereby. Molecular forces, although reduced, are still effective, however, and, if the mass be not too large or the tension too much reduced, the region of high tension will become highly curved and the regions of low tension indented in accordance with the principles already made clear, so that the fluid mass becomes elongated equatorially in a direction perpendicular to the line joining the openings of the pipettes.

"That the flowing and bulging of the drop towards the region of reduced tension is really due to gravity and not to molecular forces is readily seen from the following experiment. Saturated sodium chloride solution is poured into a glass cylinder until it approaches near to the top, and then the cylinder is inclined and distilled water poured gently down the side so as to avoid so far as possible the mixing of the two fluids. In this way we obtain a cylinder of fluid of continuously varying density increasing from above down. On now introducing into this, drops of the chloroform-oil mixture described above, we find that they float in the fluid at a little distance below the surface, where the fluid is of the same density as the drop. Under these circumstances the drop behaves as if it were weightless; only molecular forces affect it and gravity has no action upon it.[1] On now applying tenth-normal caustic soda to two poles of such a drop by means of pipettes, we find that no bulging of the drop towards the pipettes appears at all; on the contrary, the poles flatten and the equatorial region becomes highly curved, so that the drop is converted into a disk of which the long diameters are perpendicular to the line joining the orifices of the pipettes. If tenth-normal caustic soda be employed, the result is in no way different. The rationale of this phenomenon will be apparent from what has preceded."

This apparently brings the matter to the point that a mixture of olive oil and chloroform behaves one way for McClendon and another way for Robertson, in each case behaving as the experimenter thinks it should theoretically. It is a beautiful instance of how difficult it is to tell just what an experiment really shows.

Some light has been thrown on the subject by the experiments of Spek,[2] who agrees with McClendon that a drop tends to split into two drops along the line at which the surface tension is relatively highest. Spek worked both with weighted oil drops which lay on the bottom of the beaker and with drops which stayed suspended. While both kinds of drops give the same results in general, he thinks that it is more satisfactory to work with drops on the bottom of the beaker. In his first experiment he let a caustic soda solution flow out of two pipettes and impinge on opposite sides of an oil drop which had been colored with alkanna. Under these conditions the formation of a film of solid soap on the poles of the drop becomes visible, and he considers this objection-

[1] Cf. J. Plateau: "Statique des liquides soumis aux seules forces moleculaires," **2** (1873); Mach: "The Science of Mechanics," 384 (1902).

[2] Archiv Entwicklungsmechanik, **44**, 5 (1918).

able. He therefore touched opposite sides of the drop with crystals of sodium carbonate. In this way he was able to make drops of bergamot oil, of an oil used for night lights and mixed with olive oil, of castor oil, of cedar wood oil, and of pure oleic acid divide at the equator, the best results being obtained with the mixture of the night-light oil and olive oil, and with bergamot oil. When drops of mercury in dilute acid were touched at opposite points with crystals of potassium bichromate, the mercury divided along the line of highest (relative) surface tension.

Spek was also able to confirm Robertson's apparently contradictory results. "I was never able to obtain a constriction at the equator with drops of pure olive oil suspended in water. Regardless whether one touched the drop with one or with two crystals of soda, the drop always separated into a lighter and a heavier half. If one touches the drop on the right and left with soda crystals, the plane of division was always a horizontal one passing through the two poles, just as Robertson describes it. If the differences in the densities happen not to be sufficient to cause a splitting, the drop stretches in a vertical direction. The explanation of this contradictory result is undoubtedly to be found in a special behavior of the olive oil [or of the olive oil soap]. None of the other oils studied by me and not even mixtures of olive oil with other oils showed this separation into a higher half. With the other oils the effects due to differences of surface tension were not obscured by disturbing circumstances as in the case of olive oil.

"I doubt, therefore, whether McClendon used pure olive oil. If he did—and I don't know what really pure olive oil is—it had different properties from the oil used by Robertson and by me."

Without making special experiments, it is impossible to say what the difference was between the olive oil used by Robertson and Spek on the other hand and by McClendon on the other hand. It may have been a lack of free acid or a difference in stearin content. It seems to us that Spek has settled the matter satisfactorily and that a liquid drop does tend to divide along the line of the highest (relative) surface tension. Since the theory of the matter did not seem clear to Professor Chambers nearly seven years after the publication of Spek's paper, it seemed desirable to repeat some of Robertson's work.

Before describing the experiments done in the Cornell laboratory, there is another point of disagreement between Robertson and McClendon which should be mentioned. McClendon[1] says: "The mechanics of cell division may be illustrated by a more tangible model. A rubber balloon is inflated with air and attains a spherical shape. The rubber may represent the surface film and with uniform thickness of rubber we obtain uniform tension and spherical shape. If the equator of the balloon is re-inforced with a rubber band, the tension along the equator is increased and the balloon is constricted equatorially."

Robertson[2] says that McClendon forgets that a rubber balloon can in no way afford an analogy to a fluid surface because, in the first place, adjacent

[1] Archiv Entwicklungsmechanik, **34**, 265, (1912).
[2] Archiv Entwicklungsmechanik, **34**, 701 (1918).

non-continuous portions of its surface do not attract one another and, in the second place, the tension of rubber varies with the degree to which it, while that of a surface does not. The falsity[1] of this analogy has repeatedly been insisted upon by physicists."

An analogy may not be complete in every detail and perhaps never is; but that is no reason why an analogy may not be valuable. It is a reason why one must guard against falling into error when making use of an analogy; but it is quite unjustifiable to say that a rubber balloon can in no way afford an analogy to a fluid surface.

In most of the experiments done in the Cornell laboratory, advantage was taken of the technique developed by Robertson and by McClendon, but with modifications wherever necessary. For instance, McClendon used rancid olive oil, which is a bit indefinite. When olive oil has been allowed to become rancid spontaneously, one cannot be sure about the amount of free acid in a drop of oil. An insufficient amount will keep the drop from dividing rapidly; it may divide very slowly or even not at all. Consequently the oil used was made rancid artificially by adding oleic acid. Ten percent free acid was found to work very satisfactorily. Chloroform was also added, to increase the density of the drops of oil. A drop of oil was placed in a large dish of distilled water and enough sodium chloride solution added to enable the drop to be suspended. The salt solution was mixed thoroughly with the water so that there was no concentrated bottom layer.

Robertson's experiment of splitting a drop with a thread impregnated with alkali was performed first. As Robertson does it, a thread of given diameter and impregnated with a sodium hydroxide solution of a given concentration is looped around the middle of an oil drop situated at approximately half a centimeter below the surface of the water solution. The experiment is not an easy one to do, and it is rather unfortunate that such a painstaking technique was developed, for it will be shown that Robertson's experiment proves nothing whatever. This conclusion is based partly on the conviction that any experiment which can be interpreted from several antagonistic points of view is valueless in proving one to the exclusion of the others. In the first place, if on coming in contact with the impregnated thread, the drop contracts to some extent, the loop of thread must be made smaller to keep pace with the contraction or the contraction will cease and the drop will not divide. To do this and at the same time to be sure that the drop is not being cut by the thread is something of an achievement. If Robertson's technique is followed strictly, the case is much worse. On beginning the experiment Robertson tightens the loop just sufficiently to embed the impregnated thread in the drop. Inevitably a soap film is formed along the path of the thread and also below by diffusion of the alkali toward the center of the drop. The soap film dissolves and, obviously, the drop splits at least as far down as the thread. If the thread is pulled tight, so as to embed it in the drop once more, the splitting will continue and eventually the drop will split completely

[1] Cf. for example, C. M. Minchin: "Hydrostatics and Elementary Hydrokinetics," 338 (1892).

in two. Therefore Robertson's method of decreasing the surface tension of a drop at the equator may very likely cause a drop to divide; but probably surface tension has nothing whatever to do with it. Or if it has, there is no way of finding it out. But suppose the drop should divide when the thread merely touches the equator; and one is sure that the drop has not been strangled. Here an antagonist to the "equatorial theory" can suggest that a momentary bulging of the drop in the region of the equator has caused the thread to become ever so slightly embedded and the drop will divide in the manner shown above. As a matter of fact about one per cent of the number of drops experimented upon were observed to divide.

McClendon's experiment does not seem to be open to serious objections and it was the next to be tried. Here the surface tension is lowered in the region of the poles. Instead of resorting to pipettes which allow dilute caustic soda to flow against the opposite poles of the drop, glass tubes were used (inside bore 2 mm) bent into right angles and plugged with cotton at the end intended to come in contact with the drop. The tubes were filled to the same level with concentrated caustic soda solution. The ends were brought barely in contact with the poles. The caustic soda solution oozed out slowly through the cotton plugs and the drop divided, almost immediately in the majority of cases, into two equal or unequal halves without any appendages remaining as a reminiscence of a former attachment. This experiment can be performed with comparative ease once everything has been properly adjusted. There can be no question concerning its significance. A rather amusing, even perhaps a little malicious, variation of the above experiment, is interesting. If a bare thread is looped around the equator of the drop and if, at the same time, the surface tension is reduced at the poles the drop will divide in the usual way. The paradox here is that if some opponents of the "equatorial theory" feel impelled not to recognize the validity of the foregoing experiment they are called upon to explain the fact that an ordinary thread looped about the equator of an oil-drop causes the latter to divide.

But everything does not rest here. If a drop divides because the surface tension is reduced at the poles there is yet a phenomenon which remains to be demonstrated. If the drop really divides, it does so by virtue of the fact that the surface skin is stretched toward the equator since the tension is raised there. Eventually the drop is squeezed in two. Consequently, a point on the surface near a pole should be seen to move toward the equator during the process of division. If McClendon's experiment is performed in a medium containing commercial sodium chloride instead of the pure salt the phenomenon is demonstrated very easily. The commercial salt contains calcium or magnesium salts or both. These react with the caustic soda and enough calcium or magnesium base is produced to form a cap of insoluble soap at the poles of the drop. When caustic soda is applied at the poles as before, the two insoluble soap films are pulled instantly over the surface of the drop and meet in the middle to form a white equatorial band. This effect takes place to the same extent whether the drop is touched at the poles only momentarily,

so as to prevent complete division, or whether the process is allowed to go to completion. No such bad effect was observed when pure sodium chloride was used in the immersing medium.

Here it may be well to recall an experiment performed before all the others and which, although perhaps not conclusive in its results, nevertheless showed interesting possibilities. A thin-walled rubber balloon was filled with about 100 cc of distilled water. This simulated a large drop or a large cell covered with a membrane. The balloon was immersed in a three-layer liquid contained in a tall vessel. The bottom layer was carbon bisulphide, the middle one distilled water and xylene made up the top layer. The south pole of the balloon touched the carbon bisulphide layer and the north pole touched the xylene layer. Since xylene and carbon bisulphide both emulsify rubber there resulted a lowering of the surface tension at the poles of the balloon. Unfortunately, carbon bisulphide emulsifies rubber too quickly and the balloon burst. The procedure was repeated but this time xylene alone was used and now the surface tension was reduced at one pole only. After having stood for about fifteen minutes the once spherical balloon now assumed an oval shape. The apex of the oval rested on the bottom of the vessel and the wide portion rested against the xylene layer-part of the balloon being actually immersed in the layer. It should be pointed out that, notwithstanding the hydrostatic pressure, the water in the balloon was squeezed toward the region of lessened surface tension. Here was an indication that the bulging of a drop in the direction of lessened surface tension is at least not an untenable hypothesis. If this last experiment is only an indication of where the truth may lie, the insoluble soap film experiment leaves no room for doubt about where the truth does lie.

The experimental part of this manuscript was sent to Professor Chambers and Mr. Page early in 1925 and it is a pleasure to add a few paragraphs written by Mr. Page. "We are now in a position to examine the evidence as demonstrated by observation of the living cell during the act of cleavage, for and against the two theories of cellular division.

"A brief description of the process will offer a basis for comparison with the facts observed in the dividing oil drop. Not long before division occurs, the viscosity of the protoplasm decreases markedly as demonstrated by Chambers[1] with the microdissection needle, and by Heilbrunn[2] using the centrifuge method. Active Brownian movement is set up in the region of the furrow which is yet another indication of this decrease in viscosity. That this viscosity change is important as a precursor to interfacial tension changes cannot be doubted. Further, Just[3] has shown by the use of cytolysis by hypotonic solutions that the polar region becomes the point of least resistance to the osmotic bulging of the egg. Here we have an indication that the pole is the region of low resistivity. Van Beeden[4] made the interesting observation

[1] J. Exp. Zool., **23**, 483 (1917).
[2] J. Exp. Zool., **34**, 417 (1921).
[3] Am. J. Physiol., **61**, 505 (1922).
[4] Bull. Acad. roy. Belg., **41** (1883).

that the *Ascaris* egg before division shows an outward bulging to form more or less distinct lobes, almost amoeboid in aspect at the two poles. Preceding and concommitant with these phenomena the development of the two asters and spindle forming the amphiaster occurs. The egg elongates ("karyokinetic elongation") as the amphiaster attains maximum size. The cleavage furrow now cuts the karyokinetic axis at right angles. However, it does not appear essential that the aster be present inasmuch as constriction division may occur in anastral types such, for example, as noted by Farr[1] in pollen forming divisions of various dicotyledonous plants. Particularly significant to note is that a peripheral flow occurs towards and not away from the equator. Thus in *Arbacia* eggs pigment granules collect around the cleavage furrow in such a way as to demonstrate strikingly this type of viscous flow. Spek[2] especially has studied these vortical currents in many types of living eggs on division. We see that the flow is away from the area of low to one of higher tension precisely as in the oil experiment in which an insoluble calcium soap was formed at the poles. It will be recalled that in this experiment the soap cap migrated to the equator to form a white band around that region, the flow being toward the area of greater tension, namely the equator.

"Bütschli[3] in 1876 suggested that division was brought about by an increase in interfacial tension subsequent to nuclear division in the equatorial region of the egg. He subsequently elaborated this thesis with little change in the principles involved.

"We are forced to the conclusion from the preceding experimental work that the lowering of interfacial tension at the poles accounts for the division of an oil drop under the stated experimental conditions. Insofar as the dividing oil drop parallels the cleavage of the cell we may believe that similar forces are involved in this latter process. Within defined limits this physical system does mimic fission division."

The general conclusion to be drawn from this paper is that Bütschli, McClendon, and Spek were right and that Robertson was wrong. When the surface tension of a drop of liquid is lowered locally at two opposite points or poles, the drop tends to divide equatorially, along the line of highest (relative) surface tension. It is literally pinched in two by the contraction along the line of the highest (relative) surface tension and it consequently bulges at the poles, which are, by definition, the points of lowest (relative) surface tension.

In view of the abnormal results which Robertson and Spek obtained with their so-called pure olive oils and in view of the apparent effect which the nature of the soap has, these experiments should be repeated with caustic potash substituted for caustic soda or potassium carbonate substituted for sodium carbonate. It would also be well to try substituting a solid soap or a soap solution for the corresponding alkali. Although these experiments are both interesting and desirable, they are not necessary to the purpose of this paper and consequently have not been done by us.

Cornell University.

[1] Am. J. Bot., **5**, 379 (1918).
[2] Archiv. Entwicklungsmechanik, **44**, 5 (1918).
[3] Abh. Senckenberg naturforsch. Ges., **10**, (1876).

SOME PHYSICAL-CHEMICAL PROPERTIES OF MIXTURES OF ACETONE AND ISO-PROPYL ALCOHOL

BY GEORGE S. PARKS AND CLARE S. CHAFFEE

A few years ago, as a preliminary to a study of the equilibrium between acetone, hydrogen and iso-propyl alcohol, some information was needed concerning the physical-chemical properties of liquid mixtures of acetone and iso-propyl alcohol. In the absence of any such data, the investigation to be described in the present paper was undertaken. This particular study is the more interesting because of the recent investigations[1] in this laboratory of the three binary systems formed from ethyl, normal propyl, and iso-propyl alcohols.

These three binary systems were found to approximate to the requirements of an ideal or "perfect" solution to a remarkable degree. Thus the process of forming the various solutions was accompanied by a very small heat effect, the maximum ΔH values being $+4.8$, -12.7 and -10.1 calories per mole of resulting mixture in the respective cases of the ethyl-n-propyl alcohol system, the ethyl-iso-propyl alcohol system and the n-propyl-iso-propyl alcohol system. The corresponding volume changes averaged $-.025\%$, $-.010\%$ and $-.008\%$. The measured vapor pressures for the three systems agreed within the limits of experimental error with the ideal values calculated by Raoult's law. The viscosities approximated in magnitude to the requirements of Kendall's "cube-root" equation,[2] the respective deviations averaging only $+.7\%$, $-.4\%$ and $+.7\%$. All these results, of course, are not especially surprising, inasmuch as the three liquids involved are closely related alcohols of approximately the same polarity and internal pressure.

However, in the pair of substances under consideration in the present paper we have a somewhat different situation. One is an alcohol and the other a ketone, the second being the dehydrogenation product of the first. Moreover, while both liquids might be classed as moderately polar, a study of the values in Table I for dielectric constant, capillary constant, and association factor indicates that the alcohol is decidedly the more polar and the more abnormal of the two. As far as relative internal pressures are concerned, the difference is even more striking. Hence, in view of these important factors—chemical dissimilarity, different degrees of polarity, and inequality of internal pressures—it might reasonably be predicted that this binary system would exhibit marked departures from the behavior of the perfect solution. And such was found to be the case.

[1] Parks and Schwenck: J. Phys. Chem., **28**, 720 (1924); Parks and Kelley: **29**, 727 (1925); Winchester: Master's Thesis, Stanford University (1923).

[2] Kendall: J. Am. Chem. Soc., **42**, 1776 (1920).

TABLE I

	Dielectric Constant[1]	Capillary Constant[2]	Association Factor[2]	Relative Internal Pressure[3]
$(CH_3)_2CO$	21.5	1.82	1.26	1.32
$(CH_3)_2CHOH$	26.	1.05	2.86	2.49

Experimental

Purification of Substances. C. P. materials served as the starting point in preparing the acetone and iso-propyl alcohol for the present investigation. To remove possible traces of methanol and water, the C. P. acetone was treated with anhydrous calcium chloride at the rate of 200 gm. per liter. The resulting mixture was allowed to stand for several days, with occasional shaking, and was then distilled. The product thus obtained was further treated with a small quantity of anhydrous calcium chloride and carefully fractionated. The middle portion, representing about 50% of the total and boiling between 56.10° and 56.24°, was selected for use in the measurements. Its density was 0.7855 at 25°/4°, a result which compares favorably with the two values for 100% acetone, 0.7863 and 0.7849, given in the Landolt-Börnstein "Tabellen."

The iso-propyl alcohol was first dehydrated by two distillations over lime in the ordinary manner and was then carefully fractionated. The final product had a density of 0.78130 25°/4°, which corresponds to 99.8% alcohol on the basis of Brunel's value[4] of 0.78084 for 100% and the variation per 1% of water of 0.00230 obtained by Lebo.[5]

Determination of Heat of Mixing. The pure liquids thus prepared were used in making a number of mixtures, which had the designations and compositions represented in Columns 1, 2 and 3 of Table II.

In the course of the preparation of these solutions the heat of mixing was determined at an average temperature of 20° C. The method employed for this measurement was somewhat different from that described by Parks and Schwenck and should give more accurate results. In any particular determination the proper weight of the component which was to be present in greater quantity was placed in a 400 cc Dewar jar, Fig. 1, equipped with a calibrated thermometer accurate to .01°, a stirrer of the propeller type and a tightly-fitting cork cover to exclude moisture. The required weight of the other component was then placed in a small copper container, A, of about 60 cc capacity, which had a bent outlet tube extending upward from its bottom in

[1] Landolt-Börnstein-Roth-Scheel: "Tabellen," pp. 1036-1037 (1923).

[2] Ramsay and Shields: Z. physik. Chem., **12**, 468 (1893).

[3] Mortimer (J. Am. Chem. Soc., **45**, 640, 1923), gives 1.32 and 2.90 for the respective internal pressures of acetone and ethyl alcohol, relative to that of naphthalene as standard. Since Parks and Kelley found that the internal pressure of iso-propyl alcohol was, as the average of several different modes of calculation, about 14% below that of ethyl alcohol, we have accordingly reduced the value 2.90 by 14% and in this way have obtained 2.49 for iso-propyl alcohol.

[4] Brunel: J. Am. Chem. Soc., **45**, 1336 (1923).

[5] Lebo: J. Am. Chem. Soc., **43**, 1006 (1921).

such a way that it could be kept nearly full. This container occupied a position in the lower part of the Dewar jar and thus the two liquids to be mixed were brought to the same initial temperature. When this condition had been reached, the contents of the copper vessel were forced over into the Dewar jar outside by a stream of air entering the container via the upper entry tube. The air used for this purpose had been previously saturated with acetone or alcohol, as the case might be, in order to avoid any cooling effect due to vaporization within the calorimeter system. The resulting mixture was immediately stirred for two minutes at a rate of 70 R. P. M. and then allowed to stand for a similar period after which the final temperature was taken. By at once repeating the stirring and waiting interval and again reading the thermometer, the temperature correction due to stirring, heat exchanges with the surroundings, etc., was obtained. The corrected temperature change was then used for calculating the heat effect in producing one mole of the solution under consideration. This calculation was made in the usual way, by using 16 calories as the heat capacity of the calorimeter and the values of Parks and Kelley[1] for the specific heats of pure acetone and iso-propyl alcohol, respectively. The heat capacity of each mixture was taken as the sum of the heat capacities of the pure components, a procedure which is strictly accurate only in case there is no deviation from the laws of the perfect solution.

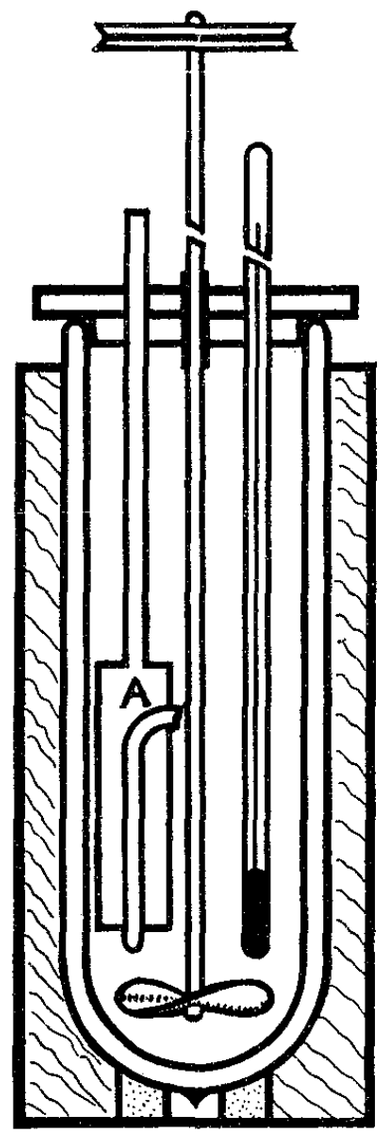


FIG. 1
The Calorimeter for the Determination of the Heats of Mixing.

The results, which are good to 5% or better, are given in Table II and are represented graphically in Fig. 2. The process of forming the various solutions took place with the absorption of considerable heat—an indication that we are dealing with solutions that are far from perfect. In the case of the equimolal mixture this heat absorption reached a maximum value of 387 calories, equivalent to a temperature lowering of 11.7°.

Densities and Refractive Indices. The densities of the liquids were next determined in the usual manner, a specific gravity bottle of 35 cc. capacity being used for this purpose. All weighings were corrected for the buoyancy of the air, and the final values appear in the second column of Table III.

[1] Parks and Kelley: J. Am. Chem. Soc., **47**, 2091 (1925).

In the formation of a perfect solution the resulting volume should be equal to the sum of the original volumes of the components involved, or in terms of densities the relationship is

$$\frac{100}{D} = \frac{1}{d_1} P_1 + \frac{1}{d_2} P_2$$

where d_1 and d_2 are the densities of the components in the pure state, P_1 and P_2 are their corresponding weight percentages in the resulting solution and D is the density of the solution. Using this equation, we have calculated the densities which appear in Column 3 of the table. These values average about 0.3% greater than the observed densities of Column 2; in other words, there is actually a very appreciable volume in crease accompanying the formation of these solutions.

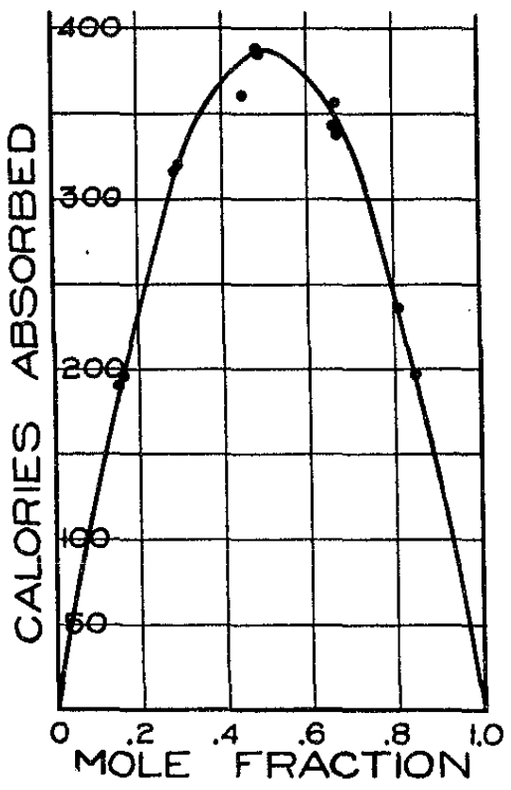


FIG. 2
Heat of Mixing plotted against Mole Fraction of Iso-Propyl Alcohol.

The refractive indices (Table III, Column 4) for sodium light were then determined with a Zeiss-Pulfrich refractometer, the method of Moore[1] for temperature measurement being employed. These observed results fall on a curve which runs below that of the values calculated on the basis of a straight-line relationship between the index of refraction and the composition by weight of the solution. Measurement of the index of refraction provides an easy and rapid method of analyzing an unknown mixture of acetone and isopropyl alcohol. As the instrument used could be read with a precision of ±1 minute and the refractive angles for the two pure substances differ by 182 minutes, the accuracy of the method is about 0.5%.

Vapor Composition at 25° C. The composition of the vapor phase in equilibrium with the solution at 25° C was next determined. This was accomplished by passing air (freed from water and carbon dioxide) through a series of three bubblers, each containing about 20 cc of the mixture under consideration. The air thus saturated with the vapor of a mixture was then passed through a condensing tube immersed in liquid air; the alcohol-acetone vapor separated out as a solid glass on the walls of this tube and, when about 1 cc of distillate had been collected, was analyzed by measurement of its refractive index. The results appear in the third column of Table IV.

[1] Moore: J. Phys. Chem., 25, 281 (1921).

TABLE II
Heat of Formation of the Mixtures at 20° C.

Liquid	Iso-Propyl Alcohol % by weight	Iso-Propyl Alcohol Mole fraction	Heat of mixing in calories per mole of mixture
1	0.00	.000	———
2A	15.65	.152	−190
2B	16.56	.161	−196
3A	30.00	.292	−316
3B	30.89	.302	−320
4A	46.34	.452	−362
4B	49.72	.486	−388
4C	49.85	.488	−385
5A	66.90	.661	−343
5B	67.41	.667	−357
5C	67.61	.669	−338
6A	81.70	.812	−236
6B	85.37	.849	−197
7	100.00	1.000	———

TABLE III
(Temperature, 25° C)

Liquid	Density Observed	Density Calculated	Refractive Index Observed	Refractive Index Calculated
1	0.7855	———	1.3555	———
2A	0.7832	0.7848	1.3578	1.3584
2B	0.7831	0.7848	1.3579	1.3586
3A	0.7818	0.7842	1.3604	1.3611
3B	0.7816	0.7842	1.3605	1.3613
4A	0.7805	0.7836	1.3634	1.3642
4B	0.7806	0.7834	1.3641	1.3649
4C	0.7807	0.7834	1.3641	1.3649
5A	0.7801	0.7827	1.3672	1.3681
6A	0.7804	0.7820	1.3708	1.3708
6B	0.7805	0.7819	1.3711	1.3715
7	0.7813	———	1.3743	———

Vapor Pressures at 25° C. The vapor pressures at 25° C were also measured in the case of several representative liquids. The method employed for this purpose was as follows. In each case a 5 cc sample of the liquid under consideration was introduced into a small bulb which was connected to a mercury manometer. The air in and above this liquid was removed by a pump consisting of activated charcoal immersed in liquid air and the bulb and manometer system were then sealed off from the outside atmosphere. During the pumping process the liquid in the bulb was protected from vaporization by its immersion in a bath of liquid air, at the temperature of which its vapor

pressure was negligible. The bulb and contents were then brought to a temperature of 25° C and the vapor pressure of the liquid was measured on the manometer by means of a cathetometer.

TABLE IV
Vapor Composition at 25° C

Liquid	Mol Fraction of Iso-Propyl Alcohol	
	In the original liquid	In the vapor
2A	.152	.108
2B	.161	.090
3A	.292	.137
3B	.302	.137
4A	.452	.172
4B	.486	.202
4C	.488	.197
5A	.661	.265
6A	.812	.390
6B	.849	.422

The results appear in Table V, Column 3. With the mixtures the results in some cases may possibly involve errors as great as 2 or 3%, owing to a residue of dissolved air in the liquid or possibly to a slight change in composition of the liquid during the pumping process. In the cases of pure acetone and pure iso-propyl alcohol these errors were entirely eliminated, since by a process of partial evaporation of the liquid all dissolved air could be pumped off without the risk of a change in composition. Our result for acetone at 25° agrees well with the value 226.3, recently obtained by Mathews[1] in a very careful investigation. For iso-propyl alcohol our present result is almost identical with that of an earlier measurement[2] in this laboratory.

TABLE V
Vapor Pressures at 25° C.

Liquid	Mole Fraction of Iso-Propyl Alcohol	Total Vapor Pressure	
		Observed	Ideal
1	.000	226.5 mm	
2B	.161	221.6 "	197.2 mm
3C	.331	190.0	166.2
4B	.486	167.2	138.0
5A	.661	139.6	106.1
6C	.825	100.0	76.1
7	1.000	44.3	

[1] Mathews: J. Am. Chem. Soc. **48**, 574 (1926).
[2] Parks and Kelley: J. Phys. Chem., **29**, 730 (1925).

For each component in a given mixture the partial pressure is simply the product of its mole fraction in the vapor phase and the total pressure of the solution. Accordingly, from the experimental data in Tables IV and V the partial pressures of the acetone and iso-propyl alcohol in the various solutions were calculated. These results appear in Columns 2 and 4 of the following table. The "ideal" pressures in all cases were derived on the assumption of Raoult's law:

$$P_A = N_A P_{oA}$$

where P_A and N_A are respectively the partial pressure and the mol fraction of component A in a given solution and P_{oA} is its vapor pressure in the pure state.

The data for the partial and total pressures are represented graphically in Fig. 3. It is obvious that the solutions show a marked positive deviation from Raoult's law, amounting in the case of an equimolal mixture to about 21%.

Viscosities. We also determined the viscosities of the various liquids, using two Oswald viscosimeters in a 25° C thermostat, regulated to .01°. The time was measured by a stop-watch. The value 0.00893 dynes per sq. cm., as obtained by Hosking,[1] was assumed for the water which was used in standardizing the instruments.

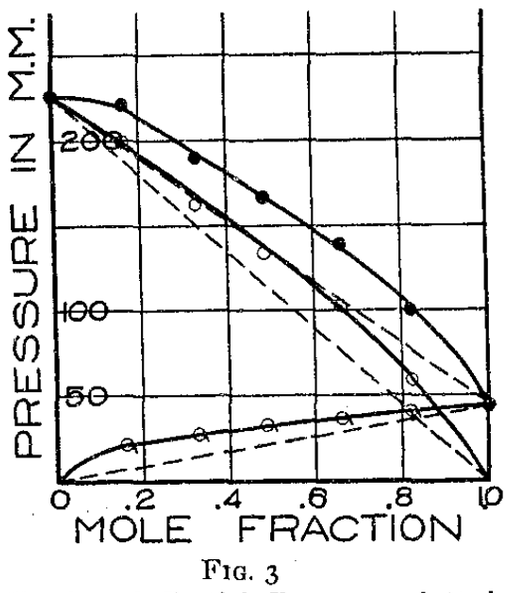


FIG. 3
Total and Partial Pressures plotted against the Mole Fraction of Iso-Propyl Alcohol.

TABLE VI
Partial Pressures at 25° C

Liquid	Partial Pressure of Acetone		Partial Pressure of Iso-Propyl Alcohol	
	Experimental	Ideal	Experimental	Ideal
1	226.5 mm	——	0.0 mm	——
2B	199.7 "	190.1 mm	21.9 "	7.1 mm
3C	162.5	151.5 "	27.5	14.7 "
4B	134.2	116.5	33.0	21.5
5A	102.6	76.8	37.0	29.3
6C	59.9	39.6	40.1	36.5
7	0.0	——	44.3	——

Comparison of the experimental results with the data calculated by Kendall's cube-root equation[2] ($\eta^{1/3} = x_1\eta_1^{1/3} + x_2\eta_2^{1/3}$, where η_1 and η_2 are the

[1] Hosking: Proc. Roy. Soc. N. S. Wales, **43**, 37 (1909).
[2] Kendall: J. Am. Chem. Soc., **42**, 1776 (1920).

viscosities of the pure components and x_1 and x_2 are their respective mole fractions) shows that the calculated values are too high on the average by 34%. As Kendall's equation has been found to give results within 0.7% of the experimental data in the case of the three alcohol mixtures previously studied, it may be considered as one of the properties of a perfect solution. On the basis of this test the present system is far from "perfect."

TABLE VII

Viscosities at 25° C (in dynes per sq. cm.)

Liquid	Observed values	Calculated values
1	.00308	———
2A	.00347	.00446
2B	.00349	———
3A	.00389	.00607
3B	.00395	———
4A	.00486	.00833
4B	.00507	———
4C	.00513	———
5A	.00703	.01205
6A	.01071	———
6B	.01187	.01622
7	.02020	———

Summary and Conclusion

Reviewing the results of the various measurements, we find that

(1) A considerable heat absorption, amounting to 387 calories per mole in the case of the equimolal mixture, takes place on formation of the several solutions.

(2) An appreciable volume increase, on the average 0.3%, accompanies the process.

(3) The measured vapor pressures and partial pressures of the resulting liquids considerably exceed the ideal values calculated by means of Raoult's law.

(4) The observed viscosities for the various solutions exhibit on the average a negative deviation of 34% from Kendall's cube-root equation.

Judging the data as a whole, we are led to the conclusion that the system under discussion is far from "perfect." In this connection it is interesting to note that the combination of deviations from the behavior of a perfect solution—heat absorption and volume increase on mixing, together with a positive deviation from Raoult's law—is entirely consistent with the findings in studies on other systems.[1] For an explanation of the present results, we have re-

[1] Hildebrand: "Solubility," p. 63 (1924). We wish to take advantage of the present opportunity to express our appreciation of Professor Hildebrand's excellent monograph. In preparing this paper we have freely used the ideas expressed therein and are indebted particularly to Chapter VII, "Causes of Deviations from Raoult's Law."

course to the great differences in association factors and relative internal pressures of acetone and iso-propyl alcohol, as shown in Table I. These differences indicate that the molecules of iso-propyl alcohol have a much greater attraction for one another than for acetone molecules or than the acetone molecules have for each other. In the pure state, therefore, the iso-propyl alcohol molecules tend largely to associate, although such association is undoubtedly indefinite and not strictly stoichiometric. On the formation of solutions with acetone, these attractive forces in the iso-propyl alcohol are weakened and as a result there is a dissociation or break-up of the more or less indefinite associated groups or "group" molecules, accompanied by an absorption of heat and an increase in volume. This decreased association as far as the alcohol is concerned leads to its positive deviation from Raoult's law in the series of solutions; while on the other hand the inherent tendency of the alcohol molecules to associate, though weakened, produces a squeezing out effect on the acetone and positive deviations for this component also. The large negative deviations of the observed viscosities from Kendall's cube-root equation can also be attributed to the lessened forces of attraction and decreased association of the iso-propyl alcohol molecules in the various solutions.

Department of Chemistry,
Stanford University, California.
October 27, 1926.

THE STUDY OF THE TANNIN-GELATIN REACTION*

BY IMO P. BAUGHMAN

Purpose of Present Work

The purpose of this investigation was: (1) to devise a method for the quantitative determination of tannin in small amounts; (2) to study the tannin-gelatin reaction in the vicinity of the maximum flocculation point; and (3) to determine the effect produced by various electrolytes and by age on this reaction.

Part I

A Colorimetric Method for Tannin

Since tannin gives characteristic color reactions with various reagents under the proper conditions, and since the quantity to be estimated is small, the possibility of a colorimetric method was alluring. Sodium hydroxide was first used but found to be unsuccessful colorimetrically. The characteristic color produced by iron salts with tannin is in many respects ideal, but the difficulty is that many of the salts are so strongly colored that their excess masks to a certain extent the characteristic color sought. The use of ferrous ammonium sulfate seemed to offer a solution of the difficulty, and an extensive study of the method was made.

A sample tannin solution containing 0.0002 gm/cc was diluted still further by adding fifteen cc of distilled water, thus producing a solution containing 0.000125 gm/cc, and then an arbitrary amount of iron reagent was added. One portion was used as a standard, and to the other the iron reagent was added dropwise to test the effect of excess reagent. A set of readings was carefully taken after each addition. If the first two readings of each set were not the same, then three to five readings were taken, and the average obtained. The accompanying graph, Fig. 1, in which readings in mm are plotted against increasing amounts of iron reagent added to a constant quantity of tannin, shows that a maximum reading is obtained beyond which an excess of the iron reagent causes no change in color.

A solution of tannin containing 0.00033 gm/cc was diluted to one-half, one-third, and one-fourth that concentration, and the resulting solutions tested as follows, the Kober type of colorimeter being used throughout this work. Table I gives the observed and calculated values in tabular form. In the column under the heading "Tannin, gm/cc," are given the amounts of tannin present in each sample as determined by dilution from the known solution. In the next column under Readings are recorded in mm the actual values obtained from the colorimeter for the samples as indicated. In the next column are given the values calculated from the preceding column. Thus

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in sample number one the more dilute solution was set at a reading of 60.0 mm. The other cup should have given a reading of 30.0 mm since the solution it contained was twice as strong as the first. Or assuming that 29.7 mm was correct then the other reading should have been twice that or 59.4 mm. Then from the actual readings taken the amount of tannin present was calculated and recorded in the last column: taking the readings 60.0 and 29.7 mm and the 0.00033 gm/cc sample as standard then,

$$0.00033 : x : : 60.0 : 29.7$$
$$x = 0.000163$$

On the other hand, using the 0.000166 gm/cc sample as standard,

$$0.000166 : x : : 29.7 : 60.0$$
$$x = 0.000335$$

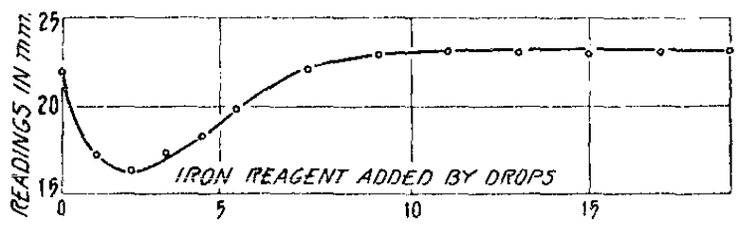


FIG. 1

TABLE I

	Actual		Calculated	
	Tannin gm/cc	Readings mm	Readings mm	Tannin gm/cc
1.	0.000330	29.7	30.0	0.000335
	0.000166	60.0	59.4	0.000163
2.	0.000330	19.9	20.0	0.000334
	0.000111	60.0	59.7	0.000109
3.	0.000330	19.9	20.0	0.000333
	0.000083	80.0	79.6	0.000082
4.	0.000330	30.1	30.0	0.000331
	0.000166	60.0	60.2	0.000166
5.	0.000330	19.8	20.0	0.000335
	0.000166	40.0	39.6	0.000163
6.	0.000330	19.8	20.0	0.000333
	0.000111	60.0	59.4	0.000109
7.	0.000330	20.1	20.0	0.000330
	0.000083	80.0	80.4	0.000083

Thus it is seen that the characteristic blue color is produced by the action of ferrous ammonium sulfate on a solution of tannin with an intensity of color which increases proportionally to the concentration of tannin, provided an excess of the iron reagent is present sufficient to react completely with all the tannin. The readings in mm, when the solutions are compared in the colorimeter, vary inversely as the concentration of tannin in the sample.

This method has been worked repeatedly for rapidity and accuracy. As a result of much experience with the method the following set of directions has been devised and found satisfactory. The iron reagent is prepared by making a saturated solution of ferrous ammonium sulfate. This solution is filtered and the resulting clear filtrate used as a stock solution. One cc of this reagent is used for a 10 cc sample of tannin solution containing not more than 0.0002 gm/cc. A concentration of tannin greater than this cannot well be used since it produces too dark a color.

Besides the iron reagent it is also necessary to have a standard solution of tannin of known concentration not to exceed 0.0002 gm/cc to which the unknown can be compared. The tannin used for solution in these experiments was Kahlbaum's purest product. Ten cc of the standard tannin solution are measured into a test tube; then a measured volume of the solution containing tannin in unknown concentration is diluted to a total volume of 10 cc (a preliminary test having previously been made to determine approximately the intensity of color); 1 cc of the iron reagent is added to each, and the two compared colorimetrically.

Experimental. Part II

Preparation and Preservation of Dilute Tannin and Gelatin Solutions for Long Periods.—One-half per cent solutions of tannin were prepared in the following manner: 5 gms. of tannin were dissolved in 1000 cc of water, boiled one-half hour, cooled, diluted to 1000 cc, poured into tall cylinders, and allowed to stand until settling was complete. Several hours later the liquid was poured into a 1000 cc glass-stoppered reagent bottle. Any very small particles still remaining soon settled and the clear supernatant liquid was drawn off by means of a pipette and diluted as desired. The bottles used for storage must be thoroughly clean and free from foreign matter, otherwise mold is liable to appear within a few days. It is an interesting fact that mold so produced is present in a concentric ring formation.

The gelatin used for the solutions in these experiments was the ordinary variety of Knox gelatin, several packages being obtained and the contents thoroughly mixed to assure as uniform material as possible. A sterile 0.5 per cent solution was prepared in the following manner: 5 gms. of gelatin were allowed to stand in 200 cc of distilled water for about 20 minutes. Then the mixture was heated until all the particles were dissolved. This was then diluted to 1 liter and the liquid introduced into a flask of one and a half liter capacity fitted with a two-hole rubber stopper, carrying in one hole a piece of glass tubing penetrating nearly to the bottom of the solution and above the stopper, which was bent like a siphon and closed at the end by a rubber tip and screw clamp; in the other hole was placed a straight calcium chloride tube so packed with absorbant cotton that air could just be forced through. The solution was heated in the flask until steam passed through the cotton, the contents being thus sterilized. Portions of the solution were obtained by opening the screw clamp and blowing through the calcium chloride tube.

This method of preparing and keeping the gelatin solutions was used very successfully. Solutions have been kept over three years and still show no evidence of mold.

The Flocculation Point of Tannin and Gelatin Solutions.—Wood[1] in working with tannin and gelatin found the greater quantity of gelatin-tannin precipitate obtained if about six times as much tannin as gelatin (in two per cent solution) was present. In 1910 Trunkel[2] reported that mutual flocculation of gelatin-tannin solutions occurs; that a point can be reached at which gelatin and tannin are both completely flocculated; and that a freshly prepared gelatin solution requires more tannin than does a twenty-four hour old gelatin solution. Thomas and Frieden report that gelatin is completely precipitated by gallotannic acid when the ratio of tannin to gelatin is not less than 2:1, and the gelatin-tannin precipitate is not soluble in excess of tannic acid; and that the ageing of gelatin solutions has no effect on the sensitivity in testing for tannin, provided bacterial action is prevented. For further literature on the Tannin-Gelatin Reaction see Thomas and Frieden.[3]

In order to determine approximately the point of maximum flocculation for tannin and gelatin solutions a set of preliminary tests was made by preparing several series of 10 cc samples of the two solutions in varying concentrations and mixing them. Since in many cases the order of addition of colloids makes a difference in their action, any possible complication from this cause was avoided by observing a definite order throughout the experiments. Each set consisted of 9 samples made up in the following way: into the first test tube was introduced 1 cc of a one-half per cent gelatin solution using a 10 cc pipette graduated in tenths; into the second, 2 cc; the third, 3 cc; and each tube in like manner up to and including the ninth. To number one was added 9 cc of a one-half per cent tannin solution; to tube number two, 8 cc of tannin; to number three, 7 cc; each tube in order being treated similarly until at the end there were nine tubes each containing 10 cc of a mixture of one-half per cent gelatin and one-half per cent tannin solutions. Each tube was inverted once only to mix thoroughly the contents and then restored to its original upright position. Flocculation occurred in each case as soon as the two solutions came into contact. After the precipitates had settled, the first five samples usually showed a clear supernatant liquid; samples six and seven were quite milky and frequently eight and nine were less milky than the preceding two. The samples were allowed to stand a few hours in order that the precipitates might settle to a certain extent, and then each sample was filtered by means of a heavy asbestos pad in a Gooch crucible.

The filtrates only were used in all cases, the precipitates being discarded. Ordinarily the first half of the series gave clear filtrates, but the following ones were milky in appearance and varying in degree from one series to another.

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[1] Dekker: "Die Gerbstoffe" p. 321.
[2] Biochem. Z., **26**, 458-493 (1910).
[3] J. Ind. Eng. Chem., **15**, 841 (1923).

The samples giving milky filtrates were also very difficult to filter. The filtrates were tested qualitatively for tannin and gelatin, the sodium hydroxide and picric acid tests being used respectively.

Table II gives typical results obtained from testing several series for the presence of tannin and gelatin.

TABLE II

	tannin present	gelatin absent
1.	" "	" "
2.	" "	" "
3.	" "	" "
4.	" "	" "
5.	" "	doubtful
6.	" "	gelatin present
7.	" "	" "
8.	" "	" "
9.	" "	" "

Tannin was thus found to be present in all the samples in each series; gelatin was found present in the latter part of the series from about samples five to nine inclusive.

TABLE III

Sample Number	Tannin gm/cc	Series A Tannin gm/cc	Ratio	Series B Tannin gm/cc	Ratio
	Original	Final		Final	
1.	0.00450	0.00134	.298	0.00126	.280
2.	0.00400	0.00099	.248	0.00104	.260
3.	0.00350	0.00077	.220	0.00076	.217
4.	0.00300	0.00045	.150	0.00045	.150
5.	0.00250	0.00024	.096	0.00027	.108
6.	0.00200	0.00023	.115	0.00029	.145
7.	0.00150	0.00033	.220	0.00031	.206
8.	0.00100	0.00019	.190	0.00021	.210
9.	0.00050	0.00013	.260	0.00013	.260
		Series C		Series D	
1.	0.00450	0.00121	.269	0.00123	.274
2.	0.00400	0.00098	.245	0.00102	.255
3.	0.00350	0.00081	.232	0.00084	.240
4.	0.00300	0.00047	.156	0.00045	.150
5.	0.00250	0.00027	.108	0.00026	.104
6.	0.00200	0.00023	.115	0.00027	.135
7.	0.00150	0.00020	.133	0.00016	.106
8.	0.00100	0.00012	.120	0.00013	.130
9.	0.00050	———	———	0.00011	.220

The quantities and concentration were happily chosen, as the apparent point of maximum flocculation is about at the middle of the series. Hence for all subsequent work the same concentration of solutions was used and the quantities made up in like series as indicated above. In order to follow the conduct of tannin-gelatin reactions many series of samples were prepared and the filtrates tested not only qualitatively for the presence of tannin and gelatin but also quantitatively for the amount of tannin using the colorimetric method devised.

Quantitative Study of the Tannin-Gelatin Reaction.—The colorimetric method described in Part I for the determination of tannin in small amounts was now used in studying the tannin-gelatin reaction. The method here was identical with that used in the preliminary qualitative work, except that the tannin in the filtrates was determined quantitatively by means of the colorimetric method described in Part I. Table III shows the analysis of the filtrates from four series of samples. The sample number is the same as the number of cc of gelatin in that particular sample and the total volume of each sample is 10 cc. In the "Ratio" column are given the ratios of tannin found in the filtrate to the tannin originally present in the sample.

From a study of these results it is seen that when tannin and gelatin are mutually flocculated, there is a point of maximum flocculation beyond which with increasing gelatin some flocculation still occurs, but a decided protective action also comes into play. The largest amount of tannin found in the filtrate is from 27 to 30 per cent of the original quantity in sample number one. The quantity decreases rapidly in the following samples to number five at which point the smallest amount of tannin is found—about 10 per cent of the original quantity. In samples six to nine inclusive the tannin content of the filtrates increases though not quite so rapidly as it decreased at the beginning of the series, about 25 per cent of the original amount remaining in the ninth sample.

The Effect of Electrolytes on Tannin-Gelatin Reactions.—The effect on tannin-gelatin reactions of electrolytes in varying concentrations was observed in the following way: a 6 per cent solution of the electrolyte was prepared, and 2 cc of this solution added to every test tube in the series of 18 samples, making in each tube a total volume of 12 cc of tannin and gelatin in varying proportions but always with a 1 per cent solution of the electrolyte present. Later a 12 per cent solution of the electrolyte was prepared, which when added to the two sets of a second series of 10 cc samples in portions of 2 cc gave a salt concentration of 2 per cent; and finally a 24 per cent solution of the electrolyte was used giving the effect of 4 per cent salt present in the dilution used. The electrolytes were chosen particularly with respect to the anions and cations to see if there was any noticeable difference in their action. Certain salts could not be used on account of interference in various ways with the necessary colorimetric tests. Barium salts had to be eliminated on account of the precipitate formed with ferrous ammonium sulfate and colored salts also could not be used on account of interference with the characteristic color of the iron tannate to be formed. The results of duplicate sets are given in Tables IV-XIII.

TABLE IV
1 per cent sodium chloride

Sample Number	Series A Tannin gm/cc Original	Series A Tannin gm/cc Final	Series A Ratio	Series B Tannin gm/cc Final	Series B Ratio
1.	0.00450	0.00123	.270	0.00112	.249
2.	0.00400	0.00110	.275	0.00094	.235
3.	0.00350	0.00050	.144	0.00044	.126
4.	0.00300	0.00032	.107	0.00027	.090
5.	0.00250	0.00017	.068	0.00015	.060
6.	0.00200	0.00027	.135	0.00030	.150
7.	0.00150	0.00018	.120	0.00024	.160
8.	0.00100	0.00014	.140	0.00015	.150
9.	0.00050	0.00012	.240	0.00014	.280

TABLE V
2 per cent sodium chloride

Sample Number	Series A Tannin gm/cc Original	Series A Tannin gm/cc Final	Series A Ratio	Series B Tannin gm/cc Final	Series B Ratio
1.	0.00450	0.00133	.296	0.00127	.282
2.	0.00400	0.00133	.332	0.00118	.295
3.	0.00350	0.00098	.280	0.00092	.263
4.	0.00300	0.00069	.230	0.00044	.146
5.	0.00250	0.00033	.132	0.00031	.124
6.	0.00200	0.00043	.215	0.00045	.225
7.	0.00150	0.00032	.213	0.00032	.213
8.	0.00100	0.00024	.240	0.00023	.230
9.	0.00050	0.00019	.380	0.00019	.380

TABLE VI
4 per cent sodium chloride

Sample Number	Series A Tannin gm/cc Original	Series A Tannin gm/cc Final	Series A Ratio	Series B Tannin gm/cc Final	Series B Ratio
1.	0.00450	0.00135	.300	0.00144	.320
2.	0.00400	0.00123	.308	0.00123	.308
3.	0.00350	0.00100	.286	0.00099	.283
4.	0.00300	0.00070	.233	0.00046	.153
5.	0.00250	0.00035	.140	0.00034	.136
6.	0.00200	0.00048	.240	0.00028	.140
7.	0.00150	0.00033	.220	0.00036	.240
8.	0.00100	0.00022	.220	0.00024	.240
9.	0.00050	0.00016	.320	0.00020	.400

TABLE VII
1 per cent sodium sulfate
Series A

Sample Number	Tannin gm/cc Original	Tannin gm/cc Final	Ratio
1.	0.00450	0.00192	.427
2.	0.00400	0.00142	.355
3.	0.00350	0.00108	.308
4.	0.00300	0.00063	.210
5.	0.00250	0.00034	.136
6.	0.00200	0.00038	.190
7.	0.00150	0.00033	.220
8.	0.00100	0.00025	.250
9.	0.00050	0.00014	.280

TABLE VIII
1 per cent magnesium chloride

Sample Number	Series A Tannin gm/cc Original	Series A Tannin gm/cc Final	Series A Ratio	Series B Tannin gm/cc Final	Series B Ratio
1.	0.00450	0.00161	.358	0.00162	.360
2.	0.00400	0.00161	.401	0.00132	.330
3.	0.00350	0.00103	.294	0.00103	.294
4.	0.00300	0.00068	.246	0.00058	.193
5.	0.00250	0.00037	.148	0.00036	.144
6.	0.00200	0.00061	.305	0.00063	.315
7.	0.00150	0.00044	.293	0.00038	.253
8.	0.00100	0.00032	.320	0.00030	.300
9.	0.00050	0.00015	.300	0.00018	.360

TABLE IX
2 per cent magnesium chloride

Sample Number	Series A Tannin gm/cc Original	Series A Tannin gm/cc Final	Series A Ratio	Series B Tannin gm/cc Final	Series B Ratio
1.	0.00450	0.00095	.211	0.00139	.309
2.	0.00400	0.00120	.300	0.00116	.290
3.	0.00350	0.00094	.268	0.00095	.272
4.	0.00300	0.00047	.156	0.00043	.143
5.	0.00250	0.00025	.100	0.00024	.096
6.	0.00200	0.00051	.255	0.00045	.225
7.	0.00150	0.00036	.240	0.00030	.200
8.	0.00100	0.00024	.240	0.00024	.240
9.	0.00050	0.00020	.400	0.00017	.340

TABLE X
4 per cent magnesium chloride

Sample Number	Series A Tannin gm/cc Original	Series A Tannin gm/cc Final	Series A Ratio	Series B Tannin gm/cc Final	Series B Ratio
1.	0.00450	0.00150	.333	0.00127	.282
2.	0.00400	0.00166	.290	0.00111	.277
3.	0.00350	0.00096	.274	0.00088	.251
4.	0.00300	0.00043	.143	0.00041	.136
5.	0.00250	0.00023	.092	0.00024	.096
6.	0.00200	0.00042	.210	0.00042	.210
7.	0.00150	0.00031	.206	0.00035	.233
8.	0.00100	0.00025	.250	0.00024	.240
9.	0.00050	0.00016	.320	0.00018	.360

TABLE XI
1 per cent aluminum chloride

Sample Number	Series A Tannin gm/cc Original	Series A Tannin gm/cc Final	Series A Ratio	Series B Tannin gm/cc Final	Series B Ratio
1.	0.00450	0.00129	.286	0.00119	.264
2.	0.00400	0.00107	.267	0.00105	.262
3.	0.00350	0.00055	.157	0.00054	.154
4.	0.00300	0.00046	.153	0.00039	.130
5.	0.00250	0.00022	.088	0.00020	.080
6.	0.00200	0.00021	.105	0.00020	.100
7.	0.00150	0.00017	.113	0.00016	.106
8.	0.00100	0.00014	.140	0.00012	.120
9.	0.00050	0.00008	.160	0.00008	.160

TABLE XII
2 per cent aluminum chloride

Sample Number	Series A Tannin gm/cc Original	Series A Tannin gm/cc Final	Series A Ratio	Series B Tannin gm/cc Final	Series B Ratio
1.	0.00450	0.00132	.294	0.00138	.307
2.	0.00400	0.00110	.275	0.00117	.292
3.	0.00350	0.00095	.272	0.00094	.268
4.	0.00300	0.00047	.156	0.00051	.170
5.	0.00250	0.00027	.108	0.00029	.116
6.	0.00200	0.00024	.120	0.00023	.115
7.	0.00150	0.00018	.120	0.00019	.126
8.	0.00100	0.00015	.150	0.00019	.190
9.	0.00050	0.00009	.180	0.00009	.180

TABLE XIII

1 per cent mercuric chloride

Sample Number	Tannin gm/cc Original	Series A Tannin gm/cc Final	Ratio	Series B Tannin gm/cc Final	Ratio
1.	0.00450	0.00150	.333	0.00169	.376
2.	0.00400	0.00132	.330	0.00133	.332
3.	0.00350	0.00093	.266	0.00079	.226
4.	0.00300	0.00050	.250	0.00073	.365
5.	0.00250	0.00037	.148	0.00052	.208
6.	0.00200	0.00027	.135	0.00029	.145
7.	0.00150	0.00024	.160	0.00025	.166
8.	0.00100	0.00020	.200	0.00019	.190
9.	0.00050	Lost		0.00013	.260

The results show that one per cent sodium chloride appreciably reduces the amount of tannin in the filtrate, while all other salts appreciably increase this amount.

The Effect of Age of Gelatin Solutions.—To find the influence of the age of a gelatin solution upon flocculation, the same tannin solution was used with gelatin solutions of different age. Sets were prepared and analyzed just as in the preceding work. The solution of gelatin used in set number one was twelve months old, and the solution used for set number two was twelve hours old. As they formed, the precipitates in the case of set number two seemed to be much heavier and whiter than those in set number one, but at the end of a few hours the two sets had much the same appearance. The precipitates were removed by filtration with Gooch crucibles and suction. Tables XIV-XV show the results.

TABLE XIV

Sample Number	Tannin gm/cc Original	Tannin gm/cc Final	Ratio	Tannin gm/cc Final	Ratio
1.	0.00450	0.00170	.378	Lost	
2.	0.00400	0.00146	.365	Lost	
3.	0.00350	0.00102	.292	0.00115	.328
4.	0.00300	0.00049	.163	0.00052	.173
5.	0.00250	0.00030	.120	0.00033	.132
6.	0.00200	0.00031	.155	0.00037	.185
7.	0.00150	0.000278	.185	0.000408	.272
8.	0.00100	0.00033	.330	0.00033	.330
9.	0.00050	0.00028	.560	0.00025	.500

Ten days later the two same gelatin solutions were used for another series of tests:

TABLE XV

Sample Number	Tannin gm/cc Original	Tannin gm/cc Final	Ratio	Tannin gm/cc Final	Ratio
1.	0.00450	0.00155	.344	0.00186	.414
2.	0.00400	0.00132	.330	0.00150	.375
3.	0.00350	0.00114	.326	0.00114	.326
4.	0.00300	0.00055	.183	0.00058	.193
5.	0.00250	0.00033	.132	0.00031	.124
6.	0.00200	0.00028	.140	0.00028	.140
7.	0.00150	0.00028	.186	0.00027	.180
8.	0.00100	0.00025	.250	0.000296	.296
9.	0.00050	0.00024	.480	0.00028	.560

These results show that age has no effect on the tannin-gelatin reaction when sterilized gelatin solutions are used. This is in accord with the findings of Thomas and Frieden.[1]

Summary and Conclusions

1. Ferrous ammonium sulfate can be used to determine tannin colorimetrically in small amounts, the method being sensitive to ±0.000005 gram per cc of tannin.

2. There is a point of maximum flocculation for one-half per cent strength tannin and gelatin solutions and beyond this point the protective action of an excess of gelatin on tannin is marked.

3. Gelatin is completely precipitated by tannin.

4. Some tannin remains in solution in all cases.

5. The highest percentage of tannin present in a one-half per cent solution is flocculated by an equal volume of a one-half per cent gelatin solution.

6. One per cent sodium chloride causes considerable decrease in the amount of tannin remaining in the filtrate.

7. The age of a sterilized gelatin solution does not affect flocculation by tannin.

Acknowledgment

This investigation was carried out in the Physical Chemistry Laboratory at Stanford University at the suggestion and under the direction of Professor S. W. Young. Acknowledgment is made for the helpful suggestions and advice of Professor Young throughout the work.

[1] J. Ind. Eng. Chem., **15**, 841 (1923).

SOCIÉTÉ DE CHIMIE INDUSTRIELLE
28, Rue St-Dominique
PARIS
(7e)

THE SOLUBILITIES AND DENSITIES OF SATURATED SOLUTIONS OF SODIUM AND POTASSIUM HALIDES AT 25°

BY ARTHUR F. SCOTT AND W. RONALD FRAZIER

In order to compute "The Changes in Volume upon Solution in Water of the Halogen Salts of the Alkali Metals," Professor G. P. Baxter[1] and his students have made an elaborate series of measurements of the densities of these solutions over a wide range of concentrations for temperatures between 0° and 100°. Only in a few cases, however, were measurements made with saturated solutions. It was the original intention of the present investigation to fill in this gap and further, to make a systematic series of solubility determinations over the same range of temperature. This work, unfortunately, has been interrupted and its completion must be postponed indefinitely; consequently, it seems desirable to publish the results which have been obtained up to the present time.

Purification of Materials

Throughout the present investigation the earlier work was taken as a model and every effort was made to attain the same degree of precision in order that the two sets of data would be on a comparable basis. Accordingly the preparation and purification of the materials used followed as nearly as possible the methods described in the second of the papers already cited. The few cases where this duplication was not possible, are noted below:

Sodium bromide and *sodium iodide* were obtained by treating recrystallized sodium carbonate with purified hydrobromic and hydriodic acids respectively. The products thus obtained were then crystallized twice in a quartz dish, and in both cases the salts were dried in an electrically heated porcelain furnace at 300° for four hours.

Silver nitrate was purified by making a saturated solution of analytically pure material which was then precipitated by the addition of an equal volume of redistilled nitric acid. The crystals were separated from the mother liquor by means of centrifuging. When dry, they were brought just to the fusion point. The solutions of this salt which were employed in the solubility determinations, were prepared immediately before they were used.

Apparatus

The Thermostat.—The solutions used in the density and solubility measurements were brought to the saturation state in a constant temperature bath. The temperature of the bath was controlled by a large, four-finger mercury-toluene regulator and was readily kept constant to within 0.01°. When in operation, the bath was maintained at 25°, the temperature being determined by a fifty-degree thermometer calibrated by the Bureau of Stand-

[1] Baxter, Boylston, Mueller, Black, and Goode: J. Am. Chem. Soc., **23**, 901 (1911); Baxter and Wallace: **38**, 70 (1916).

ards. This thermometer was graduated in tenths of a degree and could be read to hundredths. In the thermostat was also a contrivance for rotating the flasks containing the solutions to be saturated. This part of the apparatus was completely immersed in the bath.

The Flasks.—Density measurements were made by means of two ordinary 25 cc. graduated flasks, the necks of which had been constricted to secure greater accuracy in setting the meniscus. The interior diameter of the constricted portion of the neck was 2-3 mm. The volumes of the two flasks were determined by finding their water content at 25°. To accomplish this the flask was allowed to remain in the constant temperature bath until the meniscus attained a constant position, which operation usually required two to three hours. Finally the meniscus was adjusted and the neck of the flask was dried by touching it with a piece of filter paper. The flask was always weighed with a similarly treated counterpoise and both were allowed to stand in the balance case one hour before weighing. From the apparent weights of water the volumes were calculated by multiplying by the factor, 1.004001, the density of water at 25° being assumed to be 0.997071. These figures are taken directly from the paper by Baxter and Wallace. The flasks were calibrated at the beginning and at the end of the work which lasted over a period of three months. The apparent weights of the water in both cases showed a change of only 0.1 mg.; hence the volumes may be assumed to have remained constant.

Procedure

The solution to be saturated was contained in a 250 cc. bottle, the ground glass stopper of which was carefully fitted. Usually about 80 cc. of solution was made so that there would be present approximately 5 gm. of the solid salt at saturation. Particular care was taken in sealing the flask. The neck of the bottle was always completely dried before the stopper was inserted. Then the stopper was coated with paraffin and finally wired to the neck of the flask. It was found that this precaution prevented contamination from the bath and also kept the mouth of the bottle dry for subsequent operations. The bottle containing the solution was next placed in the rotating device in the thermostat and shaken for one hour, after which it was allowed to stand in the bath for one hour. With the exception of the iodides these two operations were repeated several times before the solution was used, although tests demonstrated that this repetition was superfluous.

Several methods of transferring the saturated solution to the density flask were tried and the following, which was the one finally adopted, was undoubtedly just as accurate as the others and had the advantage of being the simplest. When the solution was ready to be transferred, the bottle was held in the bath so that only the neck protruded. The glass stopper was carefully removed and replaced by a two-hole rubber stopper. In one hole of the stopper was one arm of a small, inverted glass U-tube, the bend coming just above the stopper. The arm of the tube in the saturation bottle extended almost to the bottom; its end was sealed off and a small hole was blown in the side of the tube about 1 cm. from the end. This was done in order to prevent

any crystals on the bottom of the bottle from being carried over into the density flask. The other end was drawn into a fine capillary which fitted into the constricted neck of the density flask. The second hole of the rubber stopper was provided with a small piece of glass tubing through which a slight pressure could be exerted, thereby forcing the saturated solution over into the density flask. Of course the density flask and also the transferring tube were kept in the constant temperature bath previous to use.

After the transference of the saturated solution in the above manner, the density flask was allowed to remain in the bath for about half an hour. Then the flask along with some of the water was removed from the termostat in a Dewar beaker. This Dewar beaker was transparent and slightly larger than the density flasks. With the flask thus in the beaker it was a comparatively easy matter to set the meniscus by means of small capillary tubes, an operation which required usually about a minute. Following the preliminary adjustment of the meniscus the density flask was again set in the thermostat for fifteen minutes and the meniscus was checked in the same way. When the adjustment had been found satisfactory, the neck of the flask above the constriction was wiped with a small piece of filter paper. Measurements made with a Beckmann thermometer showed that the temperature of the water in the Dewar beaker changed only 0.006° in three minutes, a variation which was less than that of the bath itself.

To correct the weight of solution to vacuum, it would have been necessary to know the exact volume at the temperature of weighing. Since this was not easy to ascertain, it was assumed that the volume was the same as at 25°. This assumption would not introduce any great error because the temperature at the time of weighing was never far from that of the bath. In all cases, therefore, the weights of solutions were corrected to vacuum by the usual formula involving terms for barometric and vapor pressures.

That the above procedure for obtaining a saturated solution and then its density is rather satisfactory, can be seen in the results of solutions of sodium chloride. In this case four different solutions prepared on four different days exhibited an extreme difference in density values of only one part in fifteen thousand.

Usually only one solution was prepared. After portions had been transferred to the two density flasks, two samples (approximately 5 cc.) were transferred to each of two tared weighing bottles. A second weighing gave, of course, the weight of the sample. These samples were next transferred carefully to one liter, glass-stoppered Erlenmeyer flasks, and diluted to about 500 cc. From the weight of the solution the weight of silver nitrate necessary to precipitate the halogen content was computed. This quantity plus an excess of about 0.5 gm. was dissolved in 150 cc. water. Then, after the salt solution had been made acid by the addition of 1 cc. of concentrated nitric acid, the silver solution was added slowly with constant stirring. The mixture was shaken and the precipitate permitted to settle over night. The precipitates obtained in this manner were next washed in order to eliminate the alkali nitrate present. In the case of the bromide and iodide precipitates the

washing was done by decantation, five times with pure water; in the case of the more soluble chloride precipitate, however, the washing was also by decantation, but first with a one percent silver nitrate solution and finally once with pure water. Following the washing the precipitates were transferred to Gooch crucibles and heated in an oven at 120° to constant weight.

Results

The data obtained in the present series of measurements are tabulated in Table I.

TABLE I

Density and Solubility Data

Salt	Weight of solution in vacuum	Volume of solution	Density	Vacuum weight of sample	Vacuum weight of AgX	Weight of salt in sample	Grams salt in 100 grams water
NaCl	30.4406	25.4105	1.19795	7.9637	5.1567	2.1029	26.406
	29.4303	24.5669	1.19797	8.2454	5.3387	2.1778	26.405
	30.4395	25.4105	1.19791				
	30.4416	25.4105	1.19799				
	Average		1.19796				26.406
NaBr	39.1782	25.4105	1.54181	6.9726	6.1866	3.3901	48.622
	37.8775	24.5669	1.54181	7.2197	6.4014	3.5080	48.590
	Average		1.54181				48.61
NaI	48.7637	25.4105	1.91904	9.9725	10.1189	6.4610	64.787
	47.1434	24.5669	1.91898	11.1807	11.3422	7.2420	64.730
	Average		1.91901				64.76
KCl	29.9301	25.4105	1.17786	7.7042	3.9070	2.0322	26.375
	28.9362	24.5669	1.17785	6.4209	3.2547	1.6929	26.365
				7.5590	3.8351	1.9948	26.389
	Average		1.17786				26.38
KBr	35.0505	25.4105	1.37937	6.5506	4.1930	2.6572	40.565
	33.8865	24.5669	1.37936	6.4546	4.1327	2.6190	40.577
	Average		1.37937				40.57
KI	43.7334	25.4105	1.72107	7.9590	6.7227	4.7533	59.723
	42.2831	24.5669	1.72114	8.3720	7.0757	5.0030	59.760
				8.4651	7.1557	5.0595	59.765
	Average		1.72111				59.75

It should be noted that the data for the iodides are less certain than those for the other salts. This is due to the fact that the saturated solutions appeared to liberate iodine on standing. For this reason the solutions were used as soon as possible after preparation.

It is of interest to compare the results presented in this paper with those given in the literature. Apparently the only density values available are those determined by Berkeley.[1] His figures for 25°, obtained by interpolation, are given below:

[1] Berkeley: Phil. Trans., **203** A, 189 (1904).

	Berkeley	S and F
NaCl	1.1978	1.19796
KCl	1.1779	1.17786

In the paper of Baxter and Wallace curves are given which show the variation of the contraction in volume per gram of salt with a change of concentration. If the contraction for a saturation solution is computed in the same way, their representative points, when plotted on the above graph, fall precisely on extensions of the proper curves. Such a figure is not presented here because of the incomplete nature of this paper.

Summary

The present communication gives values for the densities and solubilities of saturated solutions of the chlorides, bromides, and iodides of sodium and potassium at 25°.

All of the measurements recorded in this paper were made at Reed College while most of the material was prepared at Harvard University. The authors wish to acknowledge the kindness of Professor Baxter in permitting one of us to work in his laboratory during the summer of 1924. A grant from the du-Pont Fund at that time helped to defray part of the expense of the materials.

The Rice Institute.

THE IMBIBITION OF GELATIN DRIED AS A GEL AND AS A SOL*

BY ROSS AIKEN GORTNER AND WALTER F. HOFFMAN**

In an earlier paper[1] we have shown that the rate of imbibition and the extent of the imbibition of gelatin particles immersed in water is to a considerable extent dependent upon the previous treatment of the gelatin, *viz.* the concentration of the gelatin gel before drying. A gelatin prepared from a 5 per cent gel would swell faster and imbibe more water, reaching a different apparent equilibrium with water, than would a gelatin preparation dried from a 15 per cent gel.

From these experiments the conclusion was drawn that gelatin gels possessed a structure which persisted throughout the drying process and that this structure limited the volume of water which the dried particles could reimbibe. Sheppard and Elliott[2] report similar results but attribute the difference in rate of swelling to "case hardening" or surface drying effects. Our experiments, where uniform sized particles were employed, would appear to exclude differences due to surface drying changes.

The experiments described below were carried out to ascertain, if possible, whether gelatin of different concentrations, dried both as a sol and as a gel, would imbibe water at the same rate and to the same extent. It was also hoped that these experiments might throw some light upon the question as to whether the so-called sol and gel forms of gelatin actually exist as physical entities.

The gelatin sols and gels were prepared as follows. The gelatin[3] was soaked in warm water for about 30 minutes and then heated slightly in a water bath until it was an apparently uniform sol. Equal volumes of the gelatin sols were then poured into tin pie plates, and dried. Those dried as a "gel" were allowed to become rigid and then dried in a current of air at a temperature below the "melting" point. Those dried as a "sol" were placed in an electric oven and dried at 45°C. When dry, the sheets from both the sols and gels were broken into small pieces and dried for several days at 45° in an electric oven. They were then stored for use in a desiccator over calcium chloride.

For determining the rate and extent of imbibition the same technic as was used previously, was employed. About 2 gms. of the gelatin were placed in a tared Gooch crucible and the crucible was then set in a beaker of distilled water for a definite time. The crucible was then removed from the water and

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**From the Division of Agricultural Biochemistry, University of Minnesota.

[1] Gortner and Hoffman: Proc. Soc. Exp. Biol. Med., **19**, 257-264 (1922).

[2] J. Am. Chem. Soc., **44**, 373-379 (1922).

[3] The gelatin was from the same sample used in the previous study. The percentage of the gel was calculated on the basis of the air-dry gelatin, *e. g.*, a 10 percent gel means 10 grams of the air-dried gelatin plus 90 grams of water.

whirled in a centrifuge for a short time at low speed in order to remove the excess water in the crucible. The crucible and contents were then weighed and the amount of imbibed water calculated. After weighing, the crucible was again placed in the water for a definite period and again weighed in the same manner.

The results of the first series of experiments are given in Table I.

TABLE I

The Imbibition of Particles of Gelatin dried as a "Gel" and as a "Sol"

Source of Gelatin Particles	Grams water imbibed per gram dry gelatin*								
	1 hr.	2 hrs.	3 hrs.	4 hrs.	6 hrs.	8 hrs.	12 hrs.	24 hrs.	48 hrs.
Original gelatin	11.05	13.18	13.01	13.71	13.79	14.27	——	14.85	——
2.5% gelatin sol	10.93	13.33	14.03	14.26	12.70	10.02**	——	——	——
5.0% " "	7.42	8.56	9.57	10.40	10.49	10.90	——	11.18	——
10.0% " "	3.80	5.04	6.08	6.67	7.62	8.41	9.05	10.61	14.15
15.0% " "	2.95	3.91	4.56	5.30	6.20	7.10	8.30	10.13	14.16
20.0% " "	2.61	3.52	4.24	4.88	5.68	6.42	7.45	9.14	12.11
2.5% " gel	8.98	11.63	13.79	14.98	15.83	17.40	——	19.13	——
5.0% " "	6.74	8.91	10.02	11.26	11.78	12.79	——	15.33	——
10.0% " "	3.74	5.08	6.20	7.23	8.29	9.25	10.35	12.32	15.22
15.0% " "	2.76	3.94	4.97	5.97	7.25	8.37	9.89	11.85	14.36
20.0% " "	2.07	2.90	3.57	4.44	5.44	6.31	7.56	9.41	12.61

*Average of duplicate determinations. In this experiment no attempt was made to deal with uniform sized particles.

**Solating.

TABLE II

The Imbibition of Uniform Sized Particles of Gelatin dried as a "Gel" and as a "Sol"

Source of Gelatin Particles	Grams water imbibed per gram dry gelatin*							
	1 hr.	2 hrs.	3 hrs.	4 hrs.	6 hrs.	8 hrs.	12 hrs.	24 hrs.
5% gelatin sol	9.12	10.98	11.97	12.60	12.94	13.69	15.32	16.50
10% " "	3.69	5.65	6.63	7.35	8.23	9.30	10.78	12.13
15% " "	3.64	5.02	5.72	6.45	7.54	8.95	10.76	12.18
20% " "	3.64	4.89	5.73	6.44	7.60	8.70	10.10	11.32
5% " gel	7.27	9.72	10.97	11.75	12.81	14.16	17.17	18.46
10% " "	5.33	7.03	8.21	9.00	10.28	11.38	13.71	14.63
15% " "	5.32	6.70	7.59	8.48	9.12	10.52	12.10	13.35
20% " "	4.19	5.88	6.84	7.45	8.50	9.88	12.06	12.96

*Average of duplicate determinations. In this experiment the gelatin was ground to pass a 2 mm. mesh and was all retained on a 1 mm. mesh.

In the above experiment no careful attempt was made to control the size of the fragments of gelatin which were placed in the crucible. Accordingly the experiment was repeated, using dried gelatin which had been broken up

in a mortar and sieved so as to secure particles which would pass a 2 mm. sieve and be retained upon a 1 mm. sieve. The results of the experiments, using such particles, are shown in Table II. In our opinion these results are more trustworthy than are those of Table I, because of the added feature of controlled particle size.

The results where gelatin gels were employed are in general agreement with our earlier experiments. However, it is somewhat difficult to completely reconcile our earlier theory with the results which we have obtained with the gelatin sols, for with the "sol" gelatins there is also to be observed an effect of the original concentration of the sol from which the gelatin was prepared.

Certain rather striking differences between the sol and gel preparations are evident:

1. The particles from the 2.5 per cent gelatin sol (Table I) began to solate after 6 hours, whereas similar particles prepared from a 5 per cent gelatin gel showed no sign of solation at the end of 24 hours.

2. While in some instances the initial rate of imbibition appears to be higher in the case of the gelatins prepared from the sols, in every instance the amount of water imbibed at the expiration of 12, 24 and 48 hours is greater in those gelatins dried down as gels.

3. The preparations from 10 per cent, 15 per cent, and 20 per cent sols show very similar values when the particle size is controlled (Table II), whereas similar preparations from the gels show a decided progressive decrease in their imbibition rate.

4. The cause of the striking differences between the preparations from a 5 per cent sol and a 10 per cent sol (Table II) cannot be explained from the available data.

5. It will be noted that the preparation from the 5 per cent sol had a greater imbibition rate during the first six hours, but that the values for 8, 12, and 24 hours are lower than are those for the preparation from the 5 per cent gel.

It is evident from the above data that dried gelatin preparations reflect in a very considerable measure their previous history. No one theory appears to be adequate to explain this behavior, but it is our belief that the contrast between the behavior of the sol and gel preparations is at least in part due to the presence of a persistent gel structure.

It may well be that during the process of drying, the gelatin sols developed a more or less fixed structure which is reflected in the subsequent swelling curves. The existence in the dry state of a sol form which is distinct from a gel form of gelatin is neither proven nor disproven by these experiments.

NEW BOOKS

Colloid Symposium Monograph. *Edited by H. B. Weiser. Vol. IV. 23 × 16cm; pp. 378. New York: Chemical Catalog Company, 1926. Price:$6.50.* Mr. Weiser has done very good work in getting out so promptly the papers presented at the Fourth Colloid Symposium. The papers and authors are: A Survey of the Main Principles of Colloid Science, by J. W. McBain, pp. 7-18; The Colloid Particle as revealed by Catalytic Studies, by H. S. Taylor, pp. 19-28; The Water Equilibrium, by W. D. Bancroft, pp. 29-37; Making and breaking Emulsions, by W. P. Davey, pp. 38-43; Emulsification—a Study of Oil-soluble Emulsifying Agents, by Brian Mead and J. T. McCoy, pp. 44-57; The Mechanism of Adsorption and of the Swelling of Gels, by Charles Terzaghi, pp. 58-78; Specific Ion Effects in the Behavior of Tanning Agents toward Collagen treated with Neutral Salts, by K. H. Gustavson, pp. 79-101; Observations of the Colloidal Behavior of Aqueous Gelatin Systems, by E. O. Kraemer, pp. 102-121; Mass Action Effects in the Interaction of Gelatin and Acids, by W. K. Lewis and C. T. Daniell. pp. 122-131; The Helmholtz Double Layer related to Ions and Charged Particles, by E. F. Burton, pp. 132-144; X-rays and Colloids, by G. L. Clark, pp. 145-173; The Structure of Ramie Cellulose as derived from X-ray Data, by W. H. Dore and Sponsler, pp. 174-202; Organophilic Colloids, by G. S. Whitby, pp. 203-223; Colloidal Properties of the Surface of the Living Cell, by J. F. McClendon, pp. 224-233. The Function of Carbon Membranes in Osmosis, by F. E. Bartell and J. J. Osterhof, pp. 234-245; Electro-endosmose through Wood Membranes, by A. J. Stamm, pp. 246-257; The Place of Adhesion in the Gluing of Wood, by F. L. Browne and T. R. Traux, pp. 258-269; Methods for Cutting and Differential Staining of Microscopic Sections of Hardwood Glue-Joints, by A. I. Weinstein, pp. 270-280; Flocculation and Deflocculation of the Silver Halides, by S. E. Sheppard and R. H. Lambert, pp. 281-301; Pectin Jellies, by Miss G. Spencer, pp. 302-303; Cataphoresis, Electrical Charge, Critical Potential, and Stability of Colloids, by H. R. Kruyt, A. C. W. Roodvoets and P. C. van der Willigen pp. 304-310; The De-inking of Paper, by T. R. Briggs and F. H. Rhodes, pp. 311-327; The So-called Adsorption of Ferric Oxide Hydrosol by Charcoal, by A. W. Thomas and T. R. LeCompte, pp. 328-353; Ionic Antagonism in Colloid Systems, by H. B. Weiser, pp. 354-373.

It is rather a surprisingly good collection of papers and it will take some work to get together a better selection for the Fifth Colloid Symposium which is to be held at the University of Michigan in June, 1927. These meetings have been so successful that it has been thought wise to organize a Colloid Division of the American Chemical Society, under whose charge the next meeting will be held. This is as it should be. The need for these meetings has been shown and it is very desirable to have all successful efforts in chemistry at least officially part of the work of the American Chemical Society. The monographs will undoubtedly sell better when published under the auspices of the American Chemical Society, so both parties will profit by the arrangement. The Division of Chemistry of the National Research Council can now go ahead and develop some other field of activity—perhaps photochemistry.

It may be of interest to quote some passages from this volume to show how interesting it is and of what value it should be to the chemist.

"The two main problems of colloid science are structure and stability. What is the structure which places matter in this category? Whence do such structures derive such a measure of stability as to constitute nearly all the common materials met with in daily life? The answer to the first question is definitely that in most cases the unit of which colloids are built up is not the mere molecule but a higher organized unit, the particle called by Nägeli the micelle.

"The question of stability has not been properly faced. I submit that there is a class of substances whose most stable state is the colloidal condition. They are thermodynamically stable in the strictest sense, in that the colloid state is for them more stable than the crystalline or crystalloidal. Many substances have never even been brought into the

crystalloidal state, so that proof is necessarily lacking just because they are too strongly colloidal. Nevertheless there are some intermediate substances where both the colloidal and crystalloidal states are producible at will, because they are almost equally stable. This is the most important result of the study of soaps. Here we can have perfect true crystals in true reversible equilibrium with a solution in which soap exists partly as colloid and partly as crystalloid. From the standpoint of the strictest thermodynamic criteria they possess an exactly equal degree of stability. Under other conditions the colloid form is more stable and the crystal or the true crystalloidal solution passes spontaneously into the colloidal form, thereby demonstrating the lower free energy of the colloidal state for such cases. We have shown that the phase rule governs the external equilibria of all such phases.

"It is evident that this point of view embraces not only sols but also jellies and gels. If accepted, it is much more heartening than the conception, hitherto universal, that colloids are inherently unstable formations which have been brought by various devices into this state of dispersion and are rather precariously kept there, either on account of slow rate of reaction or through a balance of compensating factors which inhibit alteration," p. 7.

"In dealing with the proposed class of thermodynamically stable colloids, I would further suggest that they can only then be truly stable when the micelle has such a structure that part of every molecule of the micelle is exposed to the solvent. This idea can be best developed by illustration. For example if water and palmitic acid are sealed up in an evacuated tube the most stable and therefore permanent state is that where the palmitic acid forms a monomolecular film upon the surface of the water, any excess remaining as a crystal or crystals," p. 8.

"The Donnan distribution law appears to be of universal validity for all solutions containing electrolytes. That is, within all parts of a system in equilibrium, for example, within any colloidal solution, or within the different parts of a jelly, the product of the activities of every pair of monovalent diffusible ions must be constant. Approximately, the ionic product in terms of concentration should be constant throughout. Any change subject to a spatial constraint will cause a correspondingly redistribution of all other ions in the neighborhood, but the ionic product for each pair of free ions is constant. There is no need of a membrane. as Procter and especially Wilson have shown, to produce the constraint, although the distribution may be highly local and the constancy merely statistical.

"While therefore the Donnan distribution occurs wherever several diffusible ions are present, there is serious doubt about the numerical value of the so-called osmotic pressures (really differential pressures against solution of electrolytes) which have been obtained with colloids so far. The experimental values range from one half to tenfold those predicted. Some doubt also attaches to the "membrane potentials" because the diffusion potentials between solutions of potassium chloride and those containing a nondiffusing colloid ion have not yet been elucidated, so that opinions differ.

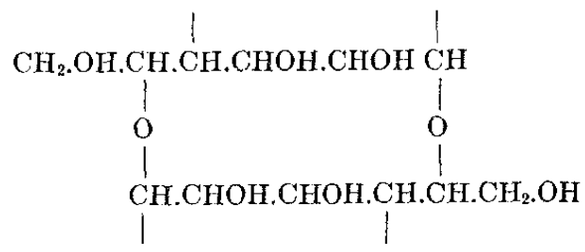
"Grossly exaggerated claims have been made by Loeb and others as to the part the Donnan equilibrium plays in colloidal behavior. Loeb's *ad hoc* definition would exclude most of the phenomena of colloids from that subject. For example the fact of gelatination or of coagulation was referred to the subject of "solubility," not of "colloidal behavior." Even in the effects he observed (his experimental results of course are not here in question) the Donnan distribution is only a factor. Two of the three or four phenomena he studied were effects of electrolytes on swelling and on viscosity. In both fields there are other instances of effects on swelling and on viscosity which exceed his tenfold in magnitude and yet cannot be ascribed to the Donnan equilibrium. For example in the case of soaps, so closely related to Loeb's materials, when the viscosity is increased fifty-fold by addition of salt the effect is comparatively enormous and it is in the opposite direction to that predicted by Loeb for salts. The other aspect of Loeb's work, which has been most useful, is his emphasis upon the predominant importance of hydrogen and hydroxyl ions. Few would care to deny chemical action between acids or bases and amino acids or their protein derivatives, but the quantitative formulation is that of sorption, and other investigators have shown that sorption of various ions is not negligible.

"The effects of Hofmeister or lyotrope (Freundlich) series of ions are too striking to be ignored. They have been observed with too many types of colloids and in connection with too many systems not even containing colloids to be attributed to systematic experimental error (Loeb). Many of the salient phenomena of reversible colloids such as coagulation by heat are profoundly affected, and often in different directions in acid and alkaline solutions. Similarly with the coagulation of reversible colloids by electrolytes, or their gelatination, or the swelling of jellies. A remarkable case in point is afforded by Michaelis' observations on the swelling of konyaku in various electrolytes. Recent workers who have fulfilled Loeb's injunction to keep the pH of their solutions constant have nevertheless observed these effects and found that sorption of these ions occurs and is specific," p. 15.

"It is significant that, in the case of formic acid decomposition, in presence of metal catalysts the reaction products are exclusively those of dehydrogenation, hydrogen and carbon dioxide, irrespective of the metal. With oxide catalysts, on the other hand, the products may be dehydrogenation as, for example, with zinc oxide, or mainly dehydration as, for example, with aluminium oxide. To what can this variation be attributed? A metal surface is composed of metal ions and electrons, an oxide surface of metal ions and oxide ions. The conclusion seems inevitable that, on the metal ion (positively charged) the dehydrogenation process occurs, whilst on the oxide ion, dehydration occurs. Attachment to the positive ion has the effect of giving the hydrogen *atoms* in the formic acid molecule greater freedom, in agreement with the observation made above that substitution by an electronegative substituent such as chlorine causes the hydrogen *ion* to have greater freedom. The negative ion causes the hydrogen atoms to be more firmly attached and so the dehydration split is favored. On this basis, *an oxide catalyst surface is to be regarded as composed, not of a single catalyst, but of two catalysts, metal ions and oxide ions and the nature of the changes induced in the adsorbed reactant is determined by the charge of the ion on which the reactant molecule is adsorbed. The extent of the two alternative changes will be determined by the relative extent of adsorption of reactant on the two ions, on the relative frequency of the two ions in the surface and on their specific individual catalytic activities. These several factors, extent of adsorption, frequency of ions in the surface and catalytic activity will be determined by the degree of saturation of the lattice ions (i. e. catalyst structure) and by the extent to which the ions are already covered by poisons (salts, ammonia, water, etc.)*. This conclusion is in good accord with the data of colloid chemistry. It is of inestimable advantage in catalytic study since it permits a forecast of catalytic phenomena," p. 25.

"Attention is called to the fact that Procter's mass action equation for the reaction of gelatin in acid implies either that the molecular weight of gelatin is not greater than double its equivalent weight, or else that all the amino groups in gelatin have the same acid strength. It is also shown that this equation breaks down completely in the face of Loeb's data obtained at low hydrogen ion concentrations. It is demonstrated that isoelectric gelatin acts as a weaker base than gelatin which has already combined with some acid. It is further pointed out that this behavior can be quantitatively explained on the assumption of internal interaction of amino groupsand carboxyl groups in the gelatin itself. A general mass action expression for the interaction of gelatin and acid is derived, including a correction term for internal compensation of the basic and acidic groups of gelatin in the neighborhood of the isoelectric point. Qualitative implications of this internal compensation's effect on the viscosity of gelatin solutions are discussed," p. 131.

"Of the various glucose formulae that come into consideration as possible structural units of cellulose, we may immediately reject the open chain aldehydic structure, since cellulose fibers normally show negligible aldehydic reactions, and consequently cannot be made up of units which contain active aldehyde groups. The possibility would remain that the structural units are straight chain, non-ring units in which the potentially aldehydic carbon atom is linked by an oxygen bridge to a carbon atom in another similar glucose unit, as in the constitutional formula proposed by Schorger.



This conception must also be rejected, however, since the C-O-C linkage would require a rectangular spacing of 2.75 Ångstrom units between chains, calculated from the sum of the atomic radii involved, whereas the X-ray data indicate definitely that the spacing between chains is 6.10 Ångstrom units in one direction and 5.40 in the other. Further grounds for the rejection of both straight chain formulae are found in the fact that a chain of six carbon atoms when fully extended cannot be accommodated in the available spacing allowed by the X-ray data.

"Turning, then, to ring formulae which involve the first carbon atom, only two of the five conceivable formulae require consideration, namely, the 1-4, or butylene oxide ring, and the 1-5, or amylene oxide ring structure. The three remaining ring formulae are highly improbable on stereochemical grounds; furthermore, carbohydrates containing such rings have not been found in nature. The possibility of their occurrence in cellulose appears to be definitely excluded by the methylation studies of Irvine and his associates, which show that the second, third and sixth positions are occupied by replaceable hydroxyls, consequently ring formation must occur through the remaining, or first, fourth and fifth positions. Other rings than the 1-4 and 1-5 are, therefore, excluded as possible units in the cellulose structure.

"Irvine and Hirst found that the glucose unit in cellulose was a stable, rather a labile form, and in accordance with conceptions then current, they regarded the unit as having the butylene oxide ring structure. Evidence has since been brought forward by Haworth and by Hirst to indicate that the normal stable form of glucose, and presumably the form which exists in cellulose, contains not a butylene oxide, but an amylene oxide ring. It will be noted that Irvine's data are equally explainable on the basis of either structure. If the unit contains a 1-5 ring instead of a 1-4 ring as was formerly supposed, then the linkage between units would be through the fourth carbon atom instead of through the fifth, but in either case the 2, 3, and 6 positions would remain open for methylation," p. 177.

"A conception of the structure of ramie cellulose is described based on previously published X-ray data and upon studies with stereochemical models. The proposed structure agrees with the space lattice indicated by the X-ray data and is apparently consistent with all of the physical properties and chemical reactions of fibrous cellulose. The cellulose structure is made up of glucose units. Of the various possible structural formulae for glucose, it is shown that the amylene oxide ring formula is in closest agreement with the X-ray requirements. It is accordingly accepted as the probable structural unit of cellulose. The glucose units are apparently united in chains of indefinite length by glucosidal condensation. The union between units is alternately a 1-1 and a 4-4 linkage. The X-ray data indicate that the 1-4 linkages, characteristic of cellobiose, do not exist in the ramie cellulose structure," p. 201.

"With a certain limited number of exceptions, solvents for the common cellulose esters are non-solvents for rubber, and, conversely, solvents for rubber are non-solvents for the cellulose esters. Speaking very broadly, the case may perhaps be stated thus: cellulose nitrate and acetate, representing a trihydric compound esterified with respectively an inorganic acid and a fatty acid of low molecular weight, are polar substances and in general imbibe and yield sols with polar organic liquids, *i. e.* with the lowest members of organic series containing active groups, while rubber, a hydrocarbon, is non-polar and in general imbibes most freely and when unvulcanized yields sols with liquids of low polarity, *i. e.*, with hydrocarbons, halogenated hydrocarbons, and the higher members of series containing active groups. In general, compounds containing active groups are swelling agents for rubber only if they contain as well hydrocarbon residues of some length; and, the larger

the hydrocarbon residue, the greater is the extent to which they are imbibed. Conversely, long hydrocarbon residues are unfavorable and active groups favorable to the dispersion of cellulose esters. Compounds containing active groups are solvents for the cellulose esters only if the hydrocarbon residue present are small. Consider the behavior of rubber and of cellulose acetate to a number of types of compounds," p. 205.

"Following the general considerations regarding the influence of the chemical constitution of liquids on the behavior of organophilic colloids which have been outlined in the above comparison of rubber and cellulose acetate, some observations were made on the behavior of metastyrene in various liquids. And it was found that this colloid, which, like rubber, is a hydrocarbon, in general swells and disperses in liquids of the same types as those in which rubber swells and fails to swell in liquids which are non-solvents for rubber but good solvents for cellulose acetate. In the case of meta-styrene, as in the case of rubber, increase in the length of the hydrocarbon residues present in a given type of organic molecule tends to increase ability to produce swelling and dispersion.

"Owing probably to the lower mechanical strength of swollen meta-styrene as compared with that of swollen rubber, meta-styrene usually disperses more easily than rubber. It was found, for example, that, where meta-styrene is insoluble in the lowest member of a given homologous series, it is not usually necessary to ascend the series so far as in the case of rubber in order to encounter a solvent. But this quantitative difference from rubber does not obscure the fact that broadly the same generalizations regarding the relation between chemical structure and swelling power hold for meta-styrene as for rubber. Some examples will serve to illustrate the parallelism between the behavior of meta-styrene and rubber and the contrast between metastyrene and cellulose acetate," p. 210.

"Consider now the question of the role of solvation in the viscosity of sols of organophilic colloids. Although the electrical charges on the particles may play a certain part in the viscosity of such sols, they apparently never play more than a comparatively small part. And the question arises as to whether the major rôle in the viscosity of sols of organophilic colloids is to be ascribed to solvation or to some other cause, such as, *e. g.*, the existence of structure in the system. In the case of sols of nitrocellulose, McBain has recently expressed the opinion that the high viscosity is due for the most part not to true solvation, but rather to the immobilization of solvents owing to its being enmeshed in a loose structure formed by cohering and ramifying rigid colloid particles or micelles. He bases this opinion in part on the fact that sorption experiments show the degree of solvation of nitrocellulose to be not more than 100 per cent of the weight of the nitrocellulose—a degree altogether too small to account for the observed viscosities.

"There is reason to believe in the case of certain other and probably in the case of many other organophilic colloid sols that the degree of solvation is much greater than that just mentioned, and consequently that solvation plays an important if not a major part in producing high viscosities. For example, rubber can readily be ascertained to imbibe 2000-4000 per cent of its weight of solvent when placed in certain liquids. When raw rubber is immersed in a liquid of high swelling power, *e. g.*, benzene, o-dichlorobenzene, carbon tetrachloride, it will be found to have increased in weight 20-40 times after 24 hours; it will thereafter gradually lose weight owing to diffusion of the swollen rubber into the liquid. And the actual degree of solvation of rubber by good swelling agents is almost certainly even higher than the increase in weight when a piece of rubber is immersed in the liquid, since diffusion of the solvated rubber out of the swollen gel begins before the piece as a whole has reached its maximum swelling," p. 218.

"Raw rubber, even when entirely free from the resin and protein which naturally accompany it, is still highly elastic. It certainly contains no free liquid phase. And it seems to me doubtful whether it can be considered as a two-phase system in the ordinary sense of the term. If different phases are in fact present, it would appear that the less rigid phase or phases can only be a part of the hydrocarbon less highly polymerized than the rest. And the chemical and physical properties of this less highly polymerized part must be so similar

to those of the more highly polymerized part that the two parts must be associated so closely, the higher polymer being, as it were, solvated by the lower, that they do not represent two separate phases in the ordinary sense of the term.

"In this connection some observations made with meta-styrene seem to be illuminating. Meta-styrene is a hard solid. In massive pieces or films it is clear; as precipitated, white. It shows no evidence of the possession of elastic properties: the films are brittle, and the powder friable. Yet it acquires elastic properties when swollen. If it is precipitated, *e. g.*, by acetone or alcohol, from a solution in, *e. g.*, xylene, benzene, or chloroform, the fresh precipitate is strikingly elastic; it is reminiscent of raw rubber; it is even more extensible than raw rubber, and it recovers from extension with a "snap". If the precipitated material is allowed to stand in the air, it gradually loses its extensibility, and when all the solvent has evaporated the remaining metastyrene is white and friable. That is to say: while in a swollen condition, meta-styrene is elastic; when unswollen, it is hard and brittle. A permanently elastic material can be obtained by incorporating with meta-styrene a non-volatile swelling agent, *e. g.*, tricresyl phosphate or isoamyl phthalate. As showing that a swollen condition is necessary for the appearance of elasticity in metastyrene, it may be mentioned that an inextensible material is obtained if, instead of a swelling agent, a non-volatile liquid without swelling properties is incorporated with meta-styrene. Such a liquid is cyclohexanol or high-boiling paraffin (*e. g.*, "Glycoline"). Both these liquids are so completely lacking in swelling power for meta-styrene that they will precipitate it from solution. And if they are incorporated with meta-styrene, the product is inelastic.

"Here then is a case of a rigid organophilic colloid which can be rendered elastic, not by causing it to form the solid phase in a solid-liquid system (the case of meta-styrene + cyclohexanol), but by merely causing it to swell. In writings on the two-phase nature of elastic gels, a solvated solid phase has been regarded as a single phase, free liquid being the other phase. "Elastified" meta-styrene is then in this accepted sense, a one-phase material.

"It would seem that, although elastic jellies, such as those from gelatin and cellulose acetate, may be two-phase systems, elastic colloids such as rubber and "elastified" meta-styrene, which are distinguished from elastic materials of the first class by their much greater elastic extensibility, are not two-phase systems, at all events in the same sense.

"The so-called plasticizers often used along with cellulose esters, with such objects as reducing brittleness and increasing flexibility, are probably "elastifiers," using this term in the sense indicated above in connection with meta-styrene; that is to say, they are non-volatile swelling agents used to improve the extensibility of the esters," p. 221.

"Valuable as the thermodynamic theory of solutions has proven to be, it has, however, given us practically no information as to the actual mechanism of osmosis. Further, with our present limited knowledge of the properties of solutions, it can aid us practically not at all in predicting the osmotic force which may be expected in systems with membranes which are not truly semipermeable and with which we have capillary effects of unknown considerable magnitudes. It is well known that osmotic flow can be obtained through membranes which are far from being strictly semi-permeable. In such systems fairly great osmotic forces are set up, and pressures of considerable magnitude are obtained, though "maximum osmotic pressure" values are never reached. In some cases we find that the operation of the osmotic force (and at least the initial direction of flow of liquid) is, in fact, opposite to that which apparently is demanded by the thermodynamic potential of the liquid system. In such cases the membranes must surely play an active part. It is, then, not surprising that osmotic theories based upon experimental results obtained with such systems as these should be different from those theories which have been obtained from systems having truly semi-permeable membranes," p. 234.

"The writers are inclined to picture conditions during the making of a glue joint in some manner such as the following: The glue, whether it be animal, casein, blood albumin, starch, or perhaps even sodium silicate, is applied to dry wood in the form of an emulsified sol of such concentration as is necessary to give a fluid of convenient consistency to spread properly with the woodworkers' machinery and to penetrate the wood cavities to some extent in order to increase the surface area available for adhesion. As already mentioned, penetration

will be obtained only if the glue wets the wood. Excessive penetration is undesirable for two reasons,—it wastes glue and may produce "starved" joints. Fortunately the dry wood absorbs water from the glue, such water penetrating to a much greater depth below the surface of the wood than the glue. A microscopic examination of sections through glue joints made with glues of alkaline reaction shows this greater penetration of the aqueous dispersion medium very beautifully, because on staining with phenolphthalein the presence of alkali can be demonstrated far beyond the limits of penetration of the glue jelly. Presumably hygroscopic moisture is drawn in still deeper than the dissolved alkalies," p. 261.

"That specific adhesion is an important factor in obtaining strong wood joints will be clear on further considering the results of the shrinkage of glue during drying. If the glue did not stick to the wood, the tendrils of jelly projecting into the wood cavities would be expected to shrivel and no longer fill the openings. The glue film between the gross surfaces would also be expected to draw away from the wood, arching over the spaces between the openings into the wood cavities. Microscopic examination proves that such is not the case. Shrinkage of the glue tendrils takes place largely by enormous exaggeration of the concave meniscus at the inner end of the tentril, leaving a film of glue clinging to the walls of the cavity. When dry the tendrils become long, hollow cylinders for a great portion of their length. Shrinkage in the main glue film evidently takes place by a decrease in total thickness, drawing the wood surfaces somewhat closer together than they were at the time the glue set," p. 265.

"In a paper given at the Colloid Symposium last year, it was shown that one very important factor for the sensitivity of photographic emulsions is the inherent substance present in the gelatin surrounding the grains. Minute traces of organic isothiocyanates and thiocarbamides in gelatin react with the silver halides to form nuclei of silver sulfide which in turn act as sensitivity centers for light decomposition of the silver halide grains. Theoretically it is therefore possible to separate the process of ripening into two distinct phases, viz., the production of silver halide grains size and composition, and having a given size distribution, and the sensitization of these by innoculation with silver sulfide," p. 281.

"Colloid chemistry of today is based entirely on the connection between the electrical charge and the stability of the colloidal particles. This relation was first discovered by Hardy, was confirmed by Burton, and was later made more definite by Powis. Measurements of the electrical surface-charge in connection with the stability of the colloidal particles are of the greatest importance and, when combined with data on the cataphoresis of colloidal solutions, must give the most needed information as to the nature of colloidal solutions. Recently one of us has shown what difficulties there are in exact measurements of cataphoresis and this paper gives chiefly the results of a study of cataphoresis in which as far as possible all objections to the technique are avoided. We have chosen the arsenious sulfide sol as the one to study, because Powis obtained results with this very sol which seemed to conflict with his theory of the critical potential, while, on the other hand, the theory described the behavior of other sols extremely well. Powis found that the critical potential, based on cataphoresis experiments in presence of potassium chloride did not agree with that which he had found with other electrolytes, such as barium chloride, aluminum chloride, thorium nitrate, etc. We first attempted to get a better agreement by avoiding, so far as possible, all the errors in the cataphoresis technique. From our results it will be seen that we have succeeded in getting a better agreement between theory and fact, but the outcome is quite different from what we had anticipated," p. 304.

"In de-inking paper the ink is dislodged from the cellulose or other fibers and is brought into suspension in a liquid medium, with which or from which it may be removed. The first stage of the process is one of dispersion, and, since the printed paper is a more or less solid complex of pigment, oil, size, and fiber, a suitable mechanical treatment (pulping) in the presence of a peptizing agent (detergent) will be necessary. In general, the peptizing agent may be an ion or a colloid in solution; the most effective detergent is a substance or a combination of substances which is able not only to peptize the carbon-black (or other pigment) of the ink, but also to emulsify, dissolve, or otherwise attack the oily vehicle of the ink and to aid in the disintegration of the paper. When brought into suspension, the carbon-black

may be removed with the liquid dispersion medium by washing the latter out of the pulp, or it may be allowed to pass into a second liquid, such as an oil, which wets carbon preferentially, or it may be adsorbed at a liquid-liquid or liquid-vapor interface and be removed by flotation. All of these methods have been tried in practice," p. 311.

"The ideal de-inking agent is probably some substance, preferably a colloid, which is adsorbed much more strongly by ink than by paper, and tends to peptize ink. If the substance is a colloid and is adsorbed more strongly by paper than by ink, a mordanting action results, which tends to bind the ink to the fiber. Such an effect has been observed with albumin," p. 326.

"Purified charcoals have been found to have no adsorbing action on iron oxide sols of the type known as Graham iron oxide sols. Technical grade charcoals have high removal powers on iron oxide sols and in this removal any adsorption effect is wholly negligible, the removal being due to the precipitating action of the electrolytes present in the charcoal as impurities," p. 353.

"If the membrane of a living cell is a colloidal film similar to a colloidal sol that can undergo reversible coagulation, there would appear to be a close analogy between the action of salt pairs in the precipitation of such sols as copper ferrocyanide and arsenious sulfide and the antagonistic action of salt pairs on the permeability and hence on the life and growth of living cells. From this point of view, all of the factors influencing the precipitating action of salt pairs as it effects the stability of sols, which I have outlined above, will be concerned in the antagonistic action of salt pairs as it affects the permeability of protoplasm," p. 372.

Wilder D. Bancroft

Handbuch der Physik. *Edited by H. Geiger and Karl Scheel. Vol. X. 26 × 17 cm; pp. viii + 486. Berlin: Julius Springer, 1926. Price: 35.40 marks, paper; 37.50 marks, bound.* This volume deals with the thermal properties of substances and is under the special editorship of F. Henning. The chapters are entitled: the solid state; fusion, freezing, and solidification; gaseous and liquid states; thermodynamics of mixtures; specific heat (theoretical part); specific heat (experimental part); determination of free energy; thermodynamics of solution.

The reviewer has found in the book a number of tables which were useful to him personally, and, doubtless, others will have similar experiences.

"If we include under the law of corresponding states those relations which follow from the identity of form of the equations of state for different substances, and if we separate from it the mechanical principle of identity, we may say that the second principle does two things. It accounts for the law of corresponding states holding and it also says that similar relations must hold in cases in which it is impossible to use the law of corresponding states in its narrower form. Most of the applications deal with the law of corresponding states in its narrower form. It has proved very useful; but it is not an absolute law and different substances show different variations," p. 196.

It was new to the reviewer that melting anethol (21.6°) or melting orthocresol (31.1°) could be used instead of melting ice in the ice calorimeter, p. 331. When one plots the difference of the atomic heats of white and gray tin divided by the temperature against the temperature, there is a tremendous maximum at about 30° abs. Measurements of specific heats down to the temperature of liquid air would be quite inadequate in showing the true form of the curve, p. 362.

"Let us call attention to the calculation of the dissociation of the fixed stars which has been made chiefly by Saha using Eggert's method. The heat of dissociation into electron and ion is known from optical observations and the specific heats of all the components are those of monatomic gases. If one used the theoretical values for the chemical constants and for the electron, one has all the data necessary for the calculation of the dissociation equilibrium. Of course the astronomical observations are not sufficient to eliminate uncertainties in the constants of the order of one. Actually we reverse the operation and calculate the temperatures of the fixed stars, which are found to be in good agreement with the values obtained in other ways," p. 391.

The book is a little vague on the vapor pressures of three-component systems, p. 456. "For the simultaneous solubility of two substances A and B in the same solvent C, a similar calculation holds. The partial vapor pressures of A and B are no longer proportional to the mol fractions. The condition of saturation gives the definite values of the vapor pressures P_1 and P_2 which are those of pure A and pure B at the temperature in question. Consequently μ_1 and μ_2 [the mol fractions] are not free to vary independently. They are therefore mutually dependent; the change in the solubility of B in presence of A determines the change of the solubility of A in presence of B."

On pp. 476 et ff. there is a supplement on time phenomena. "Since thermodynamics usually takes no cognizance of time, it deals normally with only two sets of processes: those which take place immeasurably rapidly and those which do not take place at all or take place in a time which is infinitely long so far as the thermodynamic considerations are concerned." This is a very unfortunate wording because thermodynamics does deal with no end of systems in which equilibrium is reached slowly; but we wait until equilibrium is reached before applying thermodynamics.

"As a matter of fact there are very many cases both with pure substances and with solutions, in which an assumed change does not take place practically instantaneously or in which the system does not remain unchanged in the theoretical sense during the time necessary for testing the formulas. There is often, however, the possibility in the first case of accelerating the process or of considering it accelerated by means which do not affect the thermodynamically considered state, and in the second case of retarding the change. While the full discussion of such changes or assumptions belongs under the theory of reaction velocity, we must at least point out here for what thermodynamical conceptions and relations, these things must be considered, especially in the case of solutions. . . .

"If we mix any desired amounts of hydrogen, oxygen, and water vapor at room temperature, there is practically no interaction and we are consequently dealing with three independent components. Presence of liquid has practically only the effect of causing a little of the two gases to dissolve and of giving the partial pressure of the water a practically constant value, depending on the temperature. If the water contains a small amount of colloidal platinum—which can be ignored thermodynamically—there is a slow combination of the gases to form water and the three substances can no longer be considered strictly as independently variable, though this might be considered as approximately true if the reaction takes place sufficiently slowly. If we bring the three gases to a very high temperature, the reaction runs to equilibrium very rapidly and we must consider the system thermodynamically as made up of two independently variable components and not of three. The intermediate region of slow change cannot be treated thermodynamically.

"A second case to be considered is the liquid mixture of acetaldehyde CH_3CHO and its polymer paraldehyde $(CH_3CHO)_3$. These two liquids are miscible in all proportions and act like other binary mixtures. If one adds a little sulphuric acid to the mixture, the reaction $(CH_3CHO)_3 \rightleftarrows 3CH_3CHO$ runs to equilibrium, the direction of the reaction depending on the initial relative concentrations. The solution then behaves thermodynamically like a one-component system. On distillation one gets practically pure acetaldehyde, because the paraldehyde has a much lower vapor pressure and depolymerizes as the acetaldehyde distills off. On the other hand nearly pure paraldehyde separates on freezing, because the freezing-point of the paraldehyde is more than 100° that of the acetaldehyde and this latter polymerizes as the paraldehyde separates."

Wilder D. Bancroft

Gmelins Handbuch der anorganischen Chemie. *Part I. Edited by R. J. Meyer. Eighth edition. 26 × 18 cm; pp. xli + 251. Leipzig and Berlin: Verlag Chemie, 1926.* This new edition is very welcome. The first part deals with the noble gases. After a short historical sketch and a longer one on the occurrence of the noble gases, there are chapters on the preparation, general properties, and physical properties of helium, neon, argon, krypton, xenon, and the emanations respectively. After these there are a few pages on the chemical be-

havior of the noble gases, on their detection and determination, and on their uses. The monograph does not come down to the solidification of helium, the literature being considered up to July, 1925.

"Liquid helium is extremely mobile and no increase in viscosity can be noticed even at the lowest temperatures. It has also a very low index of refraction and a very low surface tension, so that it is hard to detect the liquefaction because the meniscus runs to the wall of the vessel perfectly horizontal, as with a liquid near its critical point. It is only at temperatures below 2° abs. that the liquid shows any capillary rise against the glass wall," p. 43.

"An instable diatomic helium molecule is considered to be the cause of the band spectrum. He_2 must be constituted like He. On account of the chemical inertia of the normal helium atom, a formation of a diatomic helium gas must be due to the metastable orthohelium, which, from electron experiments, is twenty volts less than ordinary helium," p. 58.

"Kamerlingh Onnes observed that, with helium-hydrogen mixtures at temperatures at which the hydrogen has liquefied, the gaseous helium may be denser than the liquid hydrogen. We may consequently have a liquid layer floating on a gaseous one," p. 59.

"Helium diffuses slowly through tin and lead foil. Iron and palladium are still impermeable to helium at 950°, platinum at 1000°, and platinum-iridium vessels even at 1420°. On the other hand helium diffuses through quartz glass, about one percent passing through per hour at 215°, nine percent at 500°, and twenty-five percent at 1100°," p. 69.

According to Dewar the molecular heat of adsorption of helium by cocoanut charcoal is 483 cal., p. 72. Presence of mercury vapor makes some helium lines disappear while others remain in full strength. The latter belong to the parhelium spectrum while the former are all ascribed to the orthohelium spectrum. In presence of hydrogen helium can only be detected spectroscopically when it exceeds ten percent in amount, while 0.001% hydrogen can be detected in helium, p. 80.

Argon can be made to give a red, a blue, or a white spectrum, p. 152. Kirschbaum believes that the red spectrum is due to univalent argon ions and the blue spectrum chiefly to bivalent argon ions and perhaps, to some extent, to tervalent argon ions, p. 155.

Krypton consists of six isotopes and was the first element in which two isotopes differing by only one unit were observed, p. 170. The writer of the section on krypton does not believe that krypton plays any important part in the Northern Lights, p. 178. In the first place, it is believed that krypton cannot occur at the heights at which the polar lights are seen and, in the second place, the strong yellow line of krypton does not appear in the spectrum of the Northern Lights. Consequently the green krypton line cannot coincide with the green line in the aurora.

There are nine isotopes of xenon, the largest number yet found for a single element, p. 182. "The three emanations, RaEm, ThEm, and AcEm, are isotopic elements. They form colorless, chemically inert, gases, which on account of their radioactive radiation ionize the surrounding air and deposit an active precipitate of their decomposition products on all surfaces with which they are in contact. Liquid radium emanation boils at −62° and solidifies at −71°. It is colorless and transparent in transmitted light; but causes the walls of the vessel to phosphoresce, quartz glass phosphorescing blue, soda-lime glass lilac, and a potash-lead glass bluish-green," p. 199.

Neon apparently forms no hydrates; argon forms one with 4-6 mols of water. Krypton forms a definite hydrate with five of water. Xenon forms a hydrate with six or seven of water, p. 224.

The helium gas thermometer is an important instrument for low-temperature work. Liquid helium is used to give very low temperatures for the measurement of the resistance of super-metals. With liquid helium one can get down to about 1° abs. Liquid neon is used for thermostats that are to be kept at −246° to −249°. Cooper Hewitt mercury vapor lamps and Moore tubes often have argon or neon added. With a mercury vapor lamp containing 25% neon and 75% helium, the light efficiency is about double what it is with neon alone. Argon-filled incandescent lamps are a regular article of commerce. Arc recti-

fiers filled with noble gases are used with currents up to 150 amperes. Neon tubes are used to detect static charges. Nutting has recommended the use of helium tubes as light standards and the use of helium in dirigibles is very important, pp. 248-250.

Wilder D. Bancroft

Das Polarisationsmikroskop, seine Anwendung in der Kolloidforschung und in der Färberei. *By Hermann Ambronn and Albert Frey. Vol. V. 21 × 15 cm; pp.* x + *196. Leipzig: Akademische Verlagsgesellschaft, 1926. Price: 12 marks paper; 13.50 marks bound.* This book is Vol. V of the series "Kolloidforschung in Einzeldarstellungen," edited by R. Zsigmondy. Part one is devoted to a discussion of methods, in which the emphasis is on the theory of the polarization microscope and of the observations for which it is employed. After introductory chapters on the properties of light and various phenomena exhibited by optically isotropic and anisotropic substances are described in some detail. The treatment is exact and logical, with a minimum of mathematics, and dwells more on somewhat unusual features than is common in similar works. Dispersed double refraction, for instance, is treated in considerable detail and the various types of compensators are described in an exceptionally thorough manner. Dichroism, conoscopic observations, the determination of refractive indices, and the construction of the polarizing microscope are also taken up. The exposition of all this is excellent, but it is likely to be of more use to the experienced microscopist than to one who is making a first attempt to apply the polarizing microscope to his problems. The preciseness, the careful qualifications, the lack of profusion of simple diagrams, of necessity presuppose a thorough grounding in elementary "optical crystallography" to which the book offers an excellent supplement.

The second part of the work deals with double refraction phenomena of dispersoid systems; rod—and plate—double refraction are discussed in detail, as are the combinations of these with optical anisotropy inherent in the substances themselves. Strain anisotropy, flow anisotropy, and liquid crystals also are considered. Various methods of investigating the submicroscopic fine structure of dispersoid systems are given in partthree. Imbibition, applied mechanical or electrical stress, and indirect methods are explained, and the behavior of cellulose esters, zeolites, waxes, fibrous alumina, celluloid and the pleochroism of dyed fibers are interpreted in terms of the principles laid down in the preceding sections of the book.

On following through the reasoning which has been applied in the above cases, it is evident that the introductory theoretical treatment was not unduly rigorous, and that one can hardly hope to work out the explanations of new problems without such a foundation. However, there are plenty of people who are concerned primarily with the application of this knowledge, and who need not be able to derive all of it for themselves. One may utilize the change of "sign of elongation" as an indication of the degree of nitration of cellulose, strength of double refraction as an aid in the identification of textile fibers and other tissues, polarization of scattered light as a distinction between fluorescent and colloidal solutions, without bothering about the theory of the phenomena or even of the methods by which they are observed. To such persons the present work will not be particularly suggestive for it does not purport to be a manual, or a piece of propaganda for the use of the polarizing microscope. To the many workers who are trying to form a unified concept of the nature of fibers, gums and similar colloids the book presents some highly stimulating theories and methods of investigation in this field.

C. W. Mason

Lubricating Oil Salesman's Primer. *By Claude Ettele. 22 × 16 cm; pp. vi + 118. Easton: The Chemical Publishing Company, 1926. Price:* $3.00. In the preface the author says: "Lubrication is one of those common operations for which there is no adequate theory, yet it is rapidly developing into a science. Knowledge of lubrication consists of a broad knowledge of machinery and industrial processes; of bearing designs, oiling devices and lubricating systems; of the manufacture and nature of lubricants; of physical and

chemical tests which will define and identify lubricants and indicate their properties; and finally, of how lubricants perform in service. A machinery expert knows machinery and lubrication systems, a petroleum chemist is familiar with the nature of lubricants, but neither can be a successful lubricating oil salesman without experience in applying oils.

"A salesman's own experience is his most valuable asset and he is in a position to accumulate first-hand information. But a study of the experience of others is necessary to hasten his productivity. . . . It is hoped this little book will properly present a first view of the subject of lubrication and will encourage the young salesman to study advanced works without which he will be unable to develop maximum efficiency in the services of his employer and of his customers."

The subject is presented under the headings: friction and lubrication; the manufacture of lubricating oils; tests; a line of lubricants; lubrication of prime movers; lubrication of power transmission machinery; lubrication of driven machines.

The author is not a believer in the use of fixed oils, p. 14. "Oils of animal, vegetable and fish origin are called 'fixed' oils because they cannot be distilled. Originally they were the only lubricants, but the advent of mineral oils quickly displaced them to a point where now they are used only in compounds of special oils. A characteristic of fixed oils is their readiness to form emulsions when mixed with water and this is the property taken advantage of in practically all cases where they are used when compounded with mineral oils. They have, however, features desirable in lubricants; they have high heat-resisting powers in that they have high flash points and hold their body when heated, but other characteristics are not desirable in lubricants, their readiness to oxidize and form gummy deposits and their fatty acid content which corrodes metals.

"A quality of fixed oils is their so called "oiliness" which may be expressed as their ability to wet metal surfaces. This property is the basis of the loudest claims in their favor, but it is always true that for every purpose of lubrication a mineral oil can be found to render most economical service. In fact, there are some machines which would have been probably impossible to develop along their present lines were it not for the peculiar properties of mineral oils as lubricants."

"All fixed oils contain fatty acid, which when free and uncombined is corrosive. For this reason practically all specifications of spindle, machine and engine oils will contain a prohibition of any presence of animal or vegetable oils. An exception to this is the marine engine oil, the last stronghold of fixed oils as lubricants. Early types of marine engines required an oil that would emulsify and not be washed away by the large amount of water always present on early types of marine engines. At first mineral oil was used as an adulterant which adulteration increased to a point where now some well-considered marine oils contain as little as 5 per cent of a fixed oil. Marine engineers' prejudice for an emulsifying oil is rapidly decreasing, and, in fact, the use of automatic lubrication on modern marine equipment necessitates the use of mineral oil," p. 15.

Wilder D. Bancroft

Konstanten der Atomphysik. *By Walter A. Roth and Karl Scheel. 27 × 20 cm; pp. 114. Berlin: Julius Springer, 1923. Price: $2.00.* This is a separate issue in convenient form of a portion of the fifth edition of Landolt-Börnstein-Roth-Scheel: "Physikalisch-chemische Tabellen." The thirty-two tables include: atomic weights; periodic system of the elements; mixtures of isotopes in the elements; radioactive and accompanying inactive isotopes; radioactive elements; heat evolution from radioactive substances; determination of age of minerals; conversion tables for the different energy units; velocity of light in vacuo; recent determinations of N; velocity, free path, and dimensions of gas molecules; minimum thickness of films; literature on gas molecules and minimum thickness of films; values of e, of the electrochemical equivalent, and of related constants; specific charge of the electron; Planck's constant; radiation constants; wave-lengths and spectral regions for the whole spectrum; infrared wave-lengths; optical series spectra for several elements; excitation and ionization voltages for monatomic and polyatomic gases and vapors; numerical values for the "terms" in the spectrum series; absorption and scattering of Röntgen rays; crystal structures;

velocities of the ions for the most important gases and vapors; diffusion coefficients for gas ions; coefficient of mutual recombination of the ions in different gases; discharge voltages in gases; cathode drop in glow discharge; passage of electrons through matter; long-wave limit of photo-electric action; resonance wave-lengths for selective photo-electric action.

Wilder D. Bancroft

A Condensed Collection of Thermodynamic Formulas. *By P. W. Bridgman. 24 × 16 cm; pp. 34. Cambridge: Harvard University Press, 1925. Price: $1.50.* In the preface the author says: "A shorter version of the following collection of thermodynamic formulas was published in the Physical Review for April, 1914. Continued use of the formulas since then, both personally and in teaching thermodynamics, has convinced me that they are sufficiently useful to justify placing them in a more permanent and accessible form. The formulas as originally given applied only to systems for which pressure and temperature were a possible set of independent variables. An additional table is now given for the first derivatives of systems in which the pressure is a function of temperature, and temperature and volume are a possible set of independent variables. A two-phase system, such as water and steam in contact, is the most important example of such a system. I have further added a number of illustrative examples, worked in detail, to show the method of using the tables. Finally, I have discussed how in a number of cases the formulas may be extended, with very slight changes, to systems subjected to other external forces than a hydrostatic pressure, and have illustrated this extension by several examples."

The author discusses the first and second derivatives and then gives four tables: the fundamental ten quantities—notation and definitions; the first derivatives, p and τ independent variables; the first derivatives, p a function of $\tau - v$ and τ independent variables.

After this there are six pages on the use of the tables, two pages on the extension of the tables to systems in which pressure is not the only mechanical variable, and three pages on the use of the tables for other variables than P and v This last section includes the Helmholtz formula for the relation between electromotive force and heat of reaction.

This seems to the reviewer a distinctly valuable little book. It would have been a little easier on the student if the author had not made x_3 constant when writing his partial differential on p. 4 and x_1 constant when discussing it.

Wilder D. Bancroft

Edible Oils and Fats. *Their Substitutes and Adulterants. By G. D. Elsdon. 26×17 cm; pp. xix+521. London: Ernst Benn, 1926. Price: 45 shillings.* The author commences his preface with the statement that it would be difficult to write a book on the chemistry and examination of oils which is entirely different from its predecessors, and this is indeed a true saying. The realisation of a difficulty often carries one far in the overcoming of it; for it may be well said of this book that it has points of difference from almost all of the many that have been produced on this subject.

To fill about 500 pages of close print with data in a highly concentrated form is no light task, yet that is what the author has achieved—and done it well.

The book is not without its misprints and mistakes, but they are relatively few and one is much more impressed by the care with which figures, data, and references have been checked than by an odd slip here and there, such as in the mis-spelling of botanical names, and other errors mostly too obvious to be misleading.

The work is essentially a compilation and constitutes a very complete collection of the published work on the subject right up to the moment of publication; and while one is assured that the unusually large number of references has been checked from the proofs of their respective journals, the busy worker cannot fail to appreciate the wisdom of providing references to the abstracts in The Analyst and the Journal of the Society of Chemical Industry, which are so readily accessible in most laboratories.

The title "Edible Oils and Fats" is a wide one, yet the scope has been freely exceeded. Practically every known oil or fat is described, whether edible or not, including those of rare vegetable origin; while glycerine and dairy products are also dealt with.

The introduction to the book is followed by a clear and concise survey of the properties and composition of oils and fats, their individual glycerides, acids, and alcohols, with methods for the examination and separation of fatty acids.

Some thirty pages are devoted to a description of the physical tests which are usually applied to oils and fats. To those who are mainly interested in physical chemistry this may seem a small proportion of the book, but when one comes to examine this section in detail one cannot fail to admit that no physical test of importance has been omitted, while those described are, for the most part, adequately dealt with in clear and simple language. On going into details one cannot pass without comment the suggestion that the specific gravity bottle or pyknometer gives a higher degree of accuracy than is really necessary. Such a suggestion calls for a warning to the effect that the weight of liquid oils now shipped in very large bulk is calculated from a measurement of the tanks together with a very accurately-determined specific gravity.

The author has in a measure compensated for this lapse by providing a very clear drawing and specification of a delicate pyknometer and a description of its use, but no instructions given under the heading of specific gravity tell the worker precisely how to calculate the true weight in air of a litre of oil nor is he warned that, for the purpose of calculating the weight of oil, the reference standard is water at 4°C. weighed in vacuo, and that such a method is now insisted upon by keen buyers in computing the weight of a delivery of oil.

Under *Chemical Tests* one finds in many cases duplication of methods, but the thoughtful author holds out a guiding hand to the perplexed reader under the heading *Method recommended,* and offers to lead him, rightly or wrongly, in the path he himself has chosen. It is a good idea to offer advice to those who want it and, at the same time, to leave those who may know better to make their own selection.

In the matter of the many analytical constants, however, the reader must sift the grain from the chaff for himself, for the figures collected under each oil—having been taken from a wide expanse of literature—must, of necessity, include many misleading results, which results stand out from the more normal figures to the confusion of all, but against most figures will be found the observer's name—thus giving credit where it is due and relieving the author of a responsibility which a compiler is hardly called upon to bear.

The author is to be heartily congratulated upon presenting to his colleagues a truly useful work—a veritable encyclopaedia of analytical data set out in an easy form for reference. Every wise chemist concerned with the wide subject embraced should provide himself with this book, but manufacturers may find themselves less attracted. Many will be found who will not agree with many of the author's comments, but such will have to admit that they are at least the freely expressed opinions of one who is not afraid to state his thoughts, and even if they appear one-sided they are certainly not illogical and are presented in such a way as to command respect.

E. R. Bolton

Einführung in die Phasenlehre und ihre Anwendungen. *By Alexander Findlay. Second edition. Translated by Max Albert Bredig. 24 × 17 cm; pp. x + 248. Leipzig: J. A. Barth, 1925. Price: 13 gold marks.* This is Vol. VI of Bredig's "Handbuch der angewandten physikalischen Chemie" and is translated from the fifth English edition, which was reviewed in 1924 (**28**, 185). It is a pleasure to see that there is such a demand for this book in the German-reading countries.

Wilder D. Bancroft

STUDIES ON THE FORMATION OF LIESEGANG RINGS

BY PHANI BHUSAN GANGULY

In the following pages an attempt has been made to study the Liesegang phenomenon from a colloid-chemical point of view.

Peptisation plays an important part during the formation of periodic precipitates in gels. Gelatine, agar-agar, etc, which are generally used for the formation of periodic structures have, as is well known, very pronounced stabilising properties. During an experiment on the growth of Liesegang rings, say in a test-tube, the concentration of the gel is the same throughout for that experiment, consequently whatever peptising or other influences it exerts are present more or less throughout the whole mass. What however are changing from layer to layer are the concentrations of the reacting substances It thus becomes evident that in order to get a better understanding of the phenomenon, in addition to the stabilising influence of the gel, the influence of the presence of an excess of one of the reacting substances, on the nature of the newly formed substance, must be definitely known.

It is well known that the charge on a colloid particle can in many cases be traced to the presence of adsorbed ions. In certain cases by the introduction of suitable ions, the sign of the charge can be changed at will.[1] Lottermoser[2] obtained silver halide sols which were positively or negatively charged according as an excess of silver salts or of the halide salts was used. Thus the sign of the charge was directly dependent on the nature of the common ion which was present in excess and was capable of being adsorbed by the precipitate. Evidently then if silver chromate be capable of adsorbing both silver and chromate ions, one would expect the presence of an excess of either of these ions to have a distinct influence on the nature of the freshly precipitated silver chromate, it may be produced in any form from that of a coarse precipitate to that of a well dispersed colloidal sol. In the following experiments therefore, the stabilisation of the chromates of silver and lead by gelatine and agar-agar respectively, and, what seems more important, the influence of an excess of one of the reacting substances on the nature of the newly formed substances, have been studied.

An attempt has also been made to calculate the concentrations of the reacting substances at different layers of the gel, by means of a formula derived from Fick's diffusion equation in the following way.

Let us consider a column of gel of length l, with a concentrated solution of silver nitrate, say 0.5 M, diffusing into the gel from the top region OE, with a certain amount of potassium chromate uniformly distributed throughout the gel from O to F. We shall first consider the distribution of silver nitrate in the gel after any time t, neglecting for the time the presence of

[1] Cf. Mukherji: Trans. Faraday Soc., **16** (Appendix), 103 (1921).
[2] Lottermoser: J. prakt. Chem., (2) **75**, 293 (1907).

potassium chromate in the gel. Since the concentration of silver nitrate is fairly large, if t be not very great, we can reasonably suppose that the concentration of silver nitrate at O remains constant. The diffusion follows Fick's law,

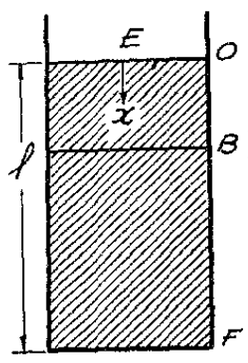


FIG. 1

$$\frac{\delta v}{\delta t} = D\frac{\delta^2 v}{\delta x^2} \qquad (1)$$

At any layer B at a distance x from the top at any time t, the concentration of silver nitrate is given by:

$$v = C\left\{1 - \frac{2}{\sqrt{\pi}}\int_0^{\frac{x}{2\sqrt{Dt}}} e^{-\xi^2}\,d\xi\right\} \qquad (2)$$

where C is the initial concentration of silver nitrate above O.

writing $$\theta(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-\xi^2}\,d\xi$$

we have from Equation (2)

$$v = C\left\{1 - \theta\left(\frac{x}{2\sqrt{Dt}}\right)\right\} \qquad (3)$$

The values of the function θ (x) for different values of x are known[1] whence the value of v for different values of x can be obtained from equation (3). Now as silver nitrate diffuses in, it reacts with the potassium chromate present and destroys the equivalent amount of the latter. Let us suppose that the concentration of the potassium chromate initially had a value A, and that silver nitrate destroys α times its weight of potassium chromate. Now let us follow the change in the concentration of the potassium chromate after a time interval t. At a distance x in time t, the amount of silver nitrate present in the gel is, from equation (3), equal to $C\left\{1 - \theta\left(\frac{x}{2\sqrt{Dt}}\right)\right\}$

This will react with the potassium chromate and thus destroy the quantity $\alpha C\left\{1 - \theta\left(\frac{x}{2\sqrt{Dt}}\right)\right\}$ of potassium chromate.

The amount of potassium chromate present at the layer D will thus be

$$A - \alpha C\left\{1 - \theta\left(\frac{x}{2\sqrt{Dt}}\right)\right\} \qquad (4)$$

This will be the amount if there were no diffusion of the potassium chromate. Actually however, the potassium chromate is diffusing simultaneously with the silver nitrate. The change in the value of A, owing to the diffusion of the potassium chromate must therefore be taken into consideration.

[1] Trans. Roy. Soc., Edinburgh, **39**, 257 (1899).

The initial condition is that the concentration of potassium chromate throughout OF is A. If OF be sufficiently long and t be small, we have at any time t,

concentration at O = o (Zero)
concentration at F = A.

The diffusion follows the Equation:

$$\frac{\delta v}{\delta t} = D_1 \frac{\delta^2 v}{x^2}$$

Solving this equation with the above mentioned conditions and evaluating the constants as in a Fourier's series, the solution is given by

$$v = \sum \frac{2A}{m\pi} e^{-\frac{D_1 m^2 \pi^2 t}{l^2}} \sin \frac{m\pi x}{l} + \frac{A}{l} x \qquad (5)$$

Now when the diffusion of potassium chromate is also taken into consideration we shall have to put the above value of v, in place of A, in equation (4) The amount of potassium chromate present at any distance x, after a time t, would thus be

$$= \left\{ \frac{2A}{\pi} \sum \frac{1}{m} e^{-\frac{D_1 m^2 \pi^2 t}{l^2}} \sin \frac{m\pi x}{l} + \frac{A}{l} x \right\} - \alpha C \left\{ 1 - \theta \left(\frac{x}{2\sqrt{Dt}} \right) \right\} \qquad (6)$$

where D_1 is the diffusion coefficient of potassium chromate. This equation has been used to calculate a series of values for the concentrations of the reacting substances at different layers of the gel, and an attempt has been made to locate the approximate positions of a few top bands by correlating these values with the experimental data obtained in this investigation.

Experimental

When a certain quantity of the stabiliser was used to peptise gradually increasing quantities of the precipitate, it was found that the change from transparent sols to turbid precipitates was not sharp eough to make it possible to determine by means of the eye the limiting concentrations corresponding to the maximum amount that can be peptised by a certain weight of the stabiliser. To get a sharp point the nephelometer devised by Kingslake[1] was used with a slight modification. The standard used was a 2% gelatine gel containing 0.05% barium sulphate. Instead of comparing the intensity of the scattered beam, the emergent beam after the incident beam had traversed a column of the liquid under examination, was compared with the standard. The observation tube was cut shorter, and a brass cap C, carrying a mirror m inclined at an angle of 45° to the emergent beam was fixed just above the observation beam. The position of the brass cap was so adjusted that the reflected beam illuminated the central slit usually occupied by the scattered beam. A slit s cut in the side of the brass cap came just in front of the mirror, and thus cut off any light likely to interfere with the standard. The arrangement is shown diagrammatically in Fig. 2.

[1] Trans. Optical Soc., (2) **26**, 53 (1923-24).

The maximum amount of precipitate which can be peptised by a certain weight of the stabiliser was first determined. The precipitates were formed by the interaction of the solutions of the respective nitrates with a potassium chromate solution. Gradually increasing volumes of the solutions of the nitrates, which were exactly equivalent to the chromate solution, were added to corresponding volumes of the chromate, the quantity of the stabiliser being the same in every case. The resulting solutions were then examined on the nephelometer. Experiments were performed with different concentrations of the gelatine. The results obtained are given in Table I, and Fig. 5. In a second series of experiments the quantities of the stabiliser and one of the reacting substances, were kept constant, the other reacting substance being added in gradually increasing quantities. The above experiments were repeated with different quantities of the stabiliser but the same amount of the reacting substances. The results are given in Tables II and III.

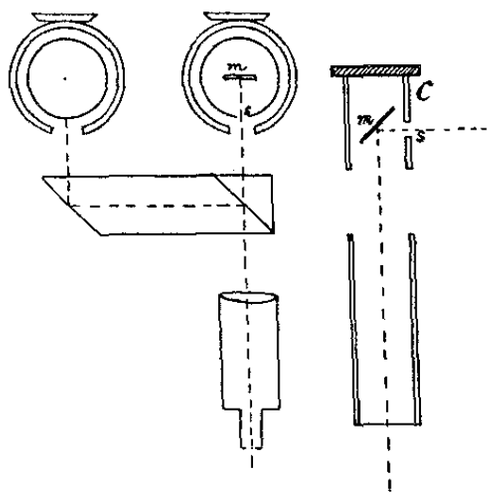


FIG. 1 FIG. 2

In the beginning the solutions were mixed by rapidly pouring from one tube into another. Various anomalous results were obtained, which were found to be due to irregular mixing, it being altogether impossible to have homogeneous mixing by any such means. With the help of the apparatus shown in Fig. 3, the solutions could be mixed simultaneously and uniformly. By means of the screw clips at c and c_1, the flow was so adjusted that the liquids from both the limbs ran out at the same time, there being no lag in the flow. Reproducible results could be easily obtained when this process of mixing was adopted.

TABLE I

10 ccs of solution containing gradually increasing amounts of $AgNO_3$ and 0.004 gm of gelatine, were each mixed with 10 ccs of exactly equivalent K_2CrO_4 solutions also containing 0.004 gm of gelatine.

	Amount of $Ag\ CrO_4$ formed	Nephelometric readings		Amount of $Ag\ CrO_4$ formed	Nephelometric readings
1.	0.0039	15.4	10.	0.0234	Very clear
2.	0.0078	15.4	11.	0.0254	Very clear
3.	0.0097	11.2	12.	0.0273	19.2
4.	0.0117	11.8	13.	0.0293	17.5
5.	0.0136	12.4	14.	0.0312	13.1
6.	0.0156	16.8	15.	0.0332	9.2
7.	0.0175	18.2	16.	0.0351	7.0
8.	0.0195	19.4	17.	0.0370	Very turbid.
9.	0.0214	Very clear	18.	0.058	Completely precipitated.

From Table I it will be seen that whereas 0.008 gram of gelatine is capable of peptising 0.25 gram of silver chromate in one case, the same amount of gelatine fails to peptise a lesser amount of the chromate viz. 0.0097 gram in another case. It thus becomes clear that peptisation by gelatine is generally dependent on the concentration of the substance peptised, in a remarkably specific way.

The scale reading of the nephelometer is a function of the turbidity of the solutions examined, a higher reading being obtained with a more transparent and consequently better peptised solution, a lower reading corresponding to a semi-transparent or partially peptised solution. If the scale readings from Table I, be plotted a curve (Fig. 4) is obtained which shows two distinct minima. These points correspond to the concentration at which the resulting mixture is more or less a precipitate, the peptising power being at its minimum. It thus becomes evident at once that there are two distinct zones for the concentrations of the reacting substances at which precipitation occurs, even when the quantity of the stabiliser present is capable of producing a transparent sol with a much larger quantity of the precipitate at a different concentration of the reacting substances.

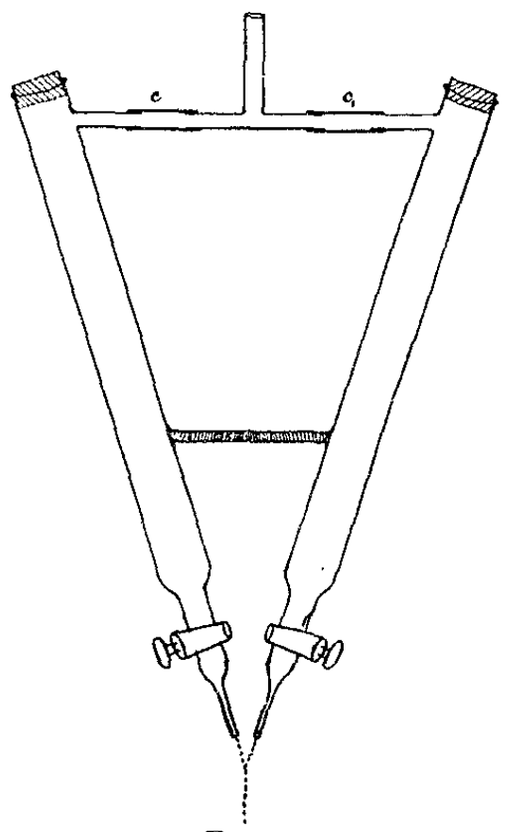


FIG. 3

In Fig. 5 are plotted the results obtained with gelatine solutions of increasing concentration, the reacting substances being mixed in equivalent quantities as before. Similar coagulation zones as in the first case are also obtained with 0.2%, 0.4%, and 0.8% gelatine solutions.

As the concentration of the gelatine solution used increased, the amount of silver chromate formed at the first coagulation zone also increased. This increase is seen clearly from Fig. 6 where the concentration of the gelatine solutions have been plotted against the amounts of silver chromate present at the coagulation zones.

Thus from the above experiments we see that there is no simple proportionality between the amount of the stabiliser and the quantity of the precipitate which it will peptise. For a gelatine solution of given concentration, two equivalent solutions producing silver chromate will have the greatest tendency to form a precipitate only when the amount of silver chromate formed has a value approximating to the quantity at the first coagulation zone or when it has a value in or beyond the second coagulation zone.

In the next series of experiments the influence of common ions on peptisation of the cromates of silver and lead by gelatine has been followed. In these

experiments the concentrations of the gelatine solution and that of one of the reacting solutions were kept fixed, the other reacting substances being added in gradually increasing quantities.

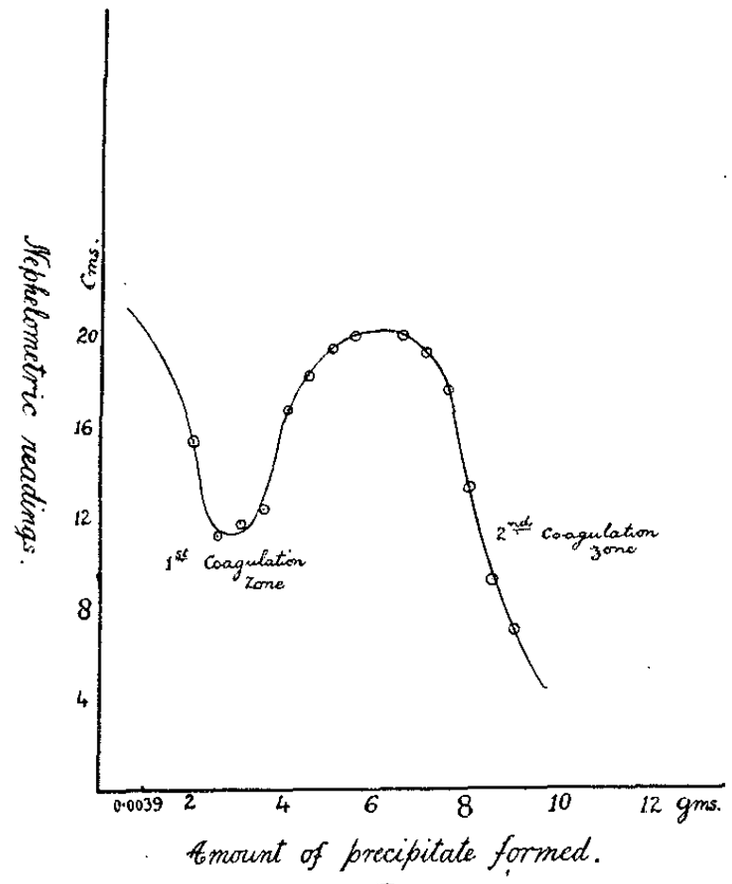


FIG. 4

In Table II the influence of an excess of silver ions is shown, the chromate ions being all used up to form silver chromate. With a 0.08% solution of gelatine there is the maximum tendency for precipitation when the quantities of the reacting solutions are nearly chemically equivalent. The precipitation

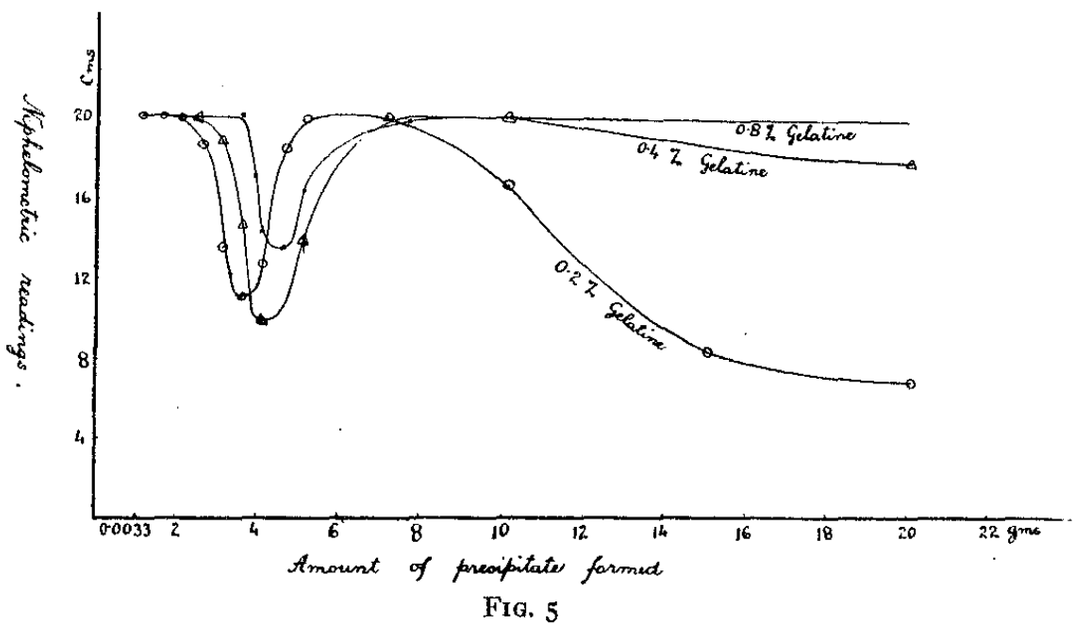


FIG. 5

continues till there is an excess of unused silver nitrate. The same weight of silver chromate viz. 0.0084 gm is formed in all mixtures, therefore if precipitation depended on the quantity of the stabiliser only, excess of silver nitrate

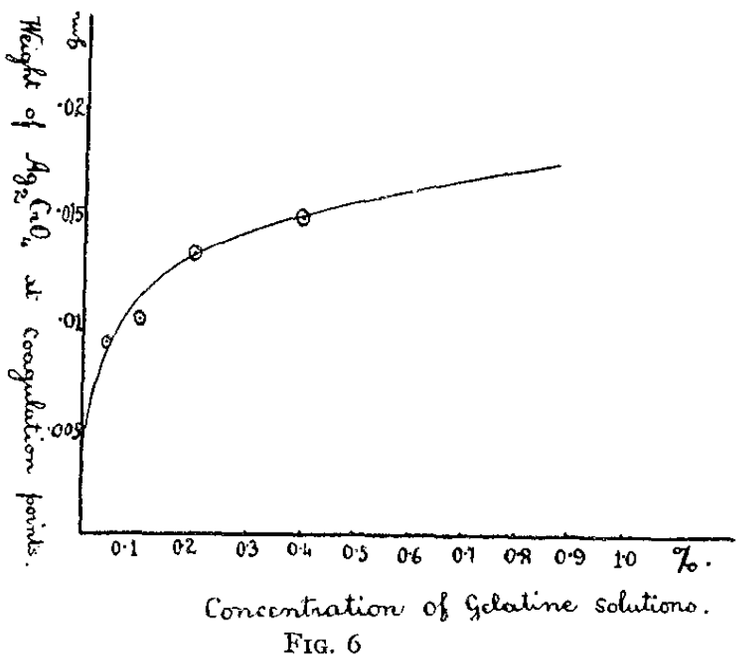


FIG. 6

TABLE II

10 ccs of solutions containing gradually increasing amounts of silver nitrate and 0.004 gram of gelatine, were each mixed with 10 ccs of solutions containing .005 gm of potassium chromate and 0.004 gm of gelatine.

Amount of silver chromate formed = 0.00843 gm.

	Excess of common ion	Nephelometric readings	Colorimetric readings		Excess of common ion	Nephelometric readings	Colorimetric readings
1.	0.0032 gm $AgNO_3$	8.4	——	7.	0.0912	Very clear	1.1 cc
2.	0.0053	14.2	——	8.	0.1912	,,	1.15 cc
3.	0.0073	18.5	——	9.	0.2912	,,	1.35 cc
4.	0.0113	Very clear	——	10.	0.5912	,,	1.4 cc
5.	0.0312	,,	1.0 cc	11.	1.1912	,,	1.5 cc
6.	0.0512	,,	1.1 cc	12.	1.3912	,,	1.9 cc

having no influence on the process of peptisation, all the subsequent mixtures as they contain the same amount of gelatine, should show the same opacity. On the contrary as the quantity of unacted silver nitrate in the mixture increases beyond a certain limit, an increase in the peptisation of the precipitate sets in, showing thereby that a certain excess of silver nitrate has a distinct stabilising influence. The quantity of free silver nitrate can be increased to an extant without any subsequent precipitation occurring. As will be seen from Table II, No. 12, the amount of silver nitrate which is left unacted upon is about 300 times the weight of silver chromate formed, but the resulting solution is still a peptised sol.

The influence of excess of chromate ions on the peptisation of silver chromate is shown in Table III. As in the above case the maximum turbidity occurs when the reacting solutions are nearly equivalent, there being very little excess of either of the reacting ions left unacted upon. Excess of unacted potassium chromate gradually brings about peptisation till for the mixture No. 8, a very clear completely peptised sol results, which does not get precipitated even when the potassium chromate is present in large quantities. Thus like the silver ions chromate ions also act as a stabiliser.

TABLE III

10 ccs of solutions containing gradually increasing amounts of K_2CrO_4 and 0.004 gram of gelatine, were each mixed with 10 ccs of solutions containing in each case 0.00875 gram of silver nitrate and 0.004 gram of gelatine.

Amount of silver chromate formed = 0.00843 gm.

	Excess of common ion	Nephelometric readings		Excess of common ion	Nephelometric readings
1.	0.002 gm of K_2CrO_4	12.0	6.	0.015	Clear
2.	0.003	12.5	7.	0.025	,,
3.	0.004	13.4	8.	0.095	,,
4.	0.005	14.5	9.	0.195	,,
5.	0.010	18.4	10.	0.495	,,

As will be seen from Table III, in presence of an excess of silver ions coagulation of the precipitate occurs only over a certain range of concentration of the free silver nitrate. This range of concentration over which the maximum turbidity occurs, however, shifts in a very remarkable way with the concentration of the gelatine used. Experiments have been performed with different concentrations of gelatine and the results are given in Table IV. An examination of the table shows that as the concentration of the gelatine solution increases, the amount of silver nitrate present at the points corresponding to the zone of maximum turbidity, also increases. Thus with a 0.05% gelatine solution the maximum turbidity occurs when there is practically no excess of silver nitrate, with a 0.08% gelatine solution, the maximum turbidity occurs in the presence of 0.00325 gm of unacted silver nitrate, and so on till finally for the 1.6% gelatine solution the maximum turbidity occurs in the presence of a relatively large amount of silver nitrate viz. 0.01 gram. It would thus mean that the stabilisation of the precipitate by silver nitrate is greatly dependent on the concentration of the gelatine solution used. For a certain weight of silver chromate as the concentration of the gelatine increases, silver nitrate up to a certain concentration seems to act as a coagulating agent, but beyond that concentration it serves to stabilise the sol, which then becomes very stable and does not get precipitated on further increase of concentration of silver nitrate.

TABLE IV

10 ccs solutions containing gradually increasing amounts of $AgNO_3$ and 4 ccs of a gelatine solution of given concentration were each mixed with 10 ccs of solutions containing 0.005 gram of K_2CrO_4 and the same amount of gelatine.

Amount of silver chromate formed = 0.00843 gm.

	Excess of common ion	Nephelometric Readings. (Concentration of gelatine solutions.)				
1.	0.00024 gm $AgNO_3$	Very turbid	11.6	Clear	Clear	Clear
2.	0.00224 "	6.8	11.4	16.8	"	"
3.	0.00325 "	7.0	10.6	15.7		
4.	0.00425 "	10.0	11.7	11.2	"	"
5.	0.00525	13.0	14.2	10.8	16.8	"
6.	0.00625	16.5	17.9	14.1	14.0	"
7.	0.00725	17.9	18.5	18.2	12.0	"
8.	0.00825	Clear	Clear	18.6	12.4	"
9.	0.00925	Clear	Clear	Clear	18.2	18.6
10.	0.01025	Clear	Clear	Clear	Clear	15.2
11.	0.01125	Clear	Clear	Clear	Clear	16.8
12.	0.02125	Clear	Clear	Clear	Clear	Very clear

It may incidentally be remarked here that the peptised sols obtained when the excess of silver ions present was beyond a certain limit, showed a gradual increase in the intensity of coloration with increase of the amount of free silver nitrate in the mixture. To follow this change a colorimetric estimation was done. All the various solutions were diluted with known volumes of water so as to bring the depth of coloration to that of one from among the series of mixtures chosen arbitrarily. The results are shown in Table II. It would be seen that, generally speaking, as the quantity of the silver nitrate increased the intensity of coloration of the solution also increased. It seems probable that as the amount of unacted silver nitrate increases, a change in the size of the peptised particle sets in, which brings about a corresponding change in the depth of coloration of the final mixtures.

The peptisation of lead chromate by agar-agar has also been followed. It will be seen from Table V, that wherever there is an excess of lead ions or an excess of neither ion, the maximum turbidity appears. When however there is an excess of chromate ions in solution, a more or less peptised sol is obtained. As the quantity of the chromate ions continually increases the sol at first gets more and more stable, but later on it gradually gets turbid, and finally gets precipitated when the quantity of chromate ions in excess becomes very large. Evidently chromate ions to a certain extent can peptise lead chromate, but lead ions do not seem to have any such peptising influence.

It can be easily shown that lead chromate adsorbs only chromate ions and not lead ions. It is well known that if a substance be precipitated in presence of such ions as it can adsorb, the precipitate can generally be subsequently peptised by washing. This has been done in a number of cases. Thus the

TABLE V

10 ccs of solutions containing different amounts of K_2CrO_4 and 0.004 gm of agar-agar, were each mixed with 10 ccs of solutions containing different amounts of $Pb(NO_3)_2$ and 0.004 gm of agar-agar.

Amount of lead chromate formed = 0.00429 gm.

	Excess of common ion present	Nephelometric readings		Excess of common ion present	Nephelometric readings
1.	0.0057 gm of $Pb(NO_3)_2$	Completely precipitated	7.	0.00028 gm of	7.4 cms
2.	0.0037 "	"	8.	0.00038 "	12.3
3.	0.0017 "	"	9.	0.00048 "	18.0
4.	0.002 "	"	10.	0.00148 "	19.1
5.	0.003 gm of K_2CrO_4	"	11.	0.00198 "	18.5
6.	0.00018 "	"	12.	0.00248 "	17.2

silver chromate precipitated in presence of an excess of either silver ions or chromate ions, could under both the circumstances be easily peptised by subsequent washing. Evidently then silver chromate is capable of adsorbing both silver ions and chromate ions. When lead chromate was precipitated in presence of an excess of lead ions, the precipitate could not be subsequently peptised at all by washing. This clearly shows that lead chromate can adsorb only chromate ions but not the lead ions. Thus it explains the ability shown by chromate ions alone, of peptising lead chromate.

The sign of the charge of the peptised silver chromate was determined in a number of cases, and in every case it was found that it was guided by the nature of the free common ion present, being positive when an excess of silver nitrate was used to peptise the sol, and being negative in presence of an excess of chromate ions. This clearly shows that peptisation by one of the reacting substances is brought about by an adsorption of one of the common ions, the resulting sol having the same charge as the adsorbed ion.

As a result therefore of the foregoing experiments one is thus led to the conclusion that a solution of silver nitrate reacting with a potassium chromate solution, will form a turbid precipitate of silver chromate only when one of the following two conditions is fulfilled:—

(1) Unless very concentrated, if the two reacting solutions be equivalent, they will be precipitated only when the quantity of silver chromate formed is a certain definite amount (which will be dependent on the concentration of the gelatine solution used.) When the quantity of silver chromate formed is either greater or smaller than this amount, a peptised solution will result.

(2) When one of the reacting substances is used in excess, for a given weight of silver chromate and a given gelatine concentration, precipitation will occur only when a certain concentration of one of the reacting substances is left in excess. If the amount of the substance left in excess be greater or less than this quantity, a peptised sol instead of a precipitate will result.

The same sort of condition will presumably hold for the case of lead chromate, but there will be the important difference that whereas in the case of silver chromate both the ions will have a peptising influence in the case of the lead chromate, lead ions will not function at all in its peptisation.

These results thus throw a great deal of light on the Liesegang phenomenon. To take the case of silver chromate rings in gelatine, as the silver nitrate diffuses into the gel, it meets the potassium chromate in all different relative concentrations. But as we have seen above precipitations will occur only in those layers where the conditions given above are fulfilled. One would thus expect the silver chromate to be formed as a precipitate in certain layers and as a peptised sol in other layers. The same will probably happen in the case of lead chromate. But in the case of lead chromate as one of the factors producing peptisation is absent viz. the peptising influence of the lead ions, the frequency of occurence of the precipitate layers will be greater, which seems to be quite in accordance with the actual experimental structures obtained with lead chromate in gelatine gels. It appears now that it will be interesting to calculate the distribution of concentrations of silver nitrate and potassium chromate in different layers of the gel. By using Equation (6) a series of values have been calculated and are given in the following table. The value of D_1, the diffusion coefficient of K_2CrO_4, could not be found in any of the usual tables. It has been calculated by using Nernst's equation viz,

$$D = RT\frac{2uv}{u+v}$$

which when expressed in C. G. S. units gives

$$D = 0.04485\frac{uv}{u+v}[1 + 0.0034\ (t - 18)].$$

(cf. Nernst: "Theoretical Chemistry," pp. 435.)

Taking $t = 12°$, $u = 64.5$, and $v = 72$,[1] we get the value of $D_1 = 1.49$ for a dilute viz a M/300 (about 0.0065%) solution of potassium chromate. The value of D, the diffusion coefficient of silver nitrate, has been obtained by plotting the values of Thovert[2] for different concentrations of silver nitrate. The value for a 0.5 M (8.49%) solution of silver nitrate is thus found from the curve to be 0.933. These values of D and D_1 have been used in the following calculations.

The series $\sum \frac{1}{m} e - \frac{D_1 m^2 \pi^2 t}{l^2} \sin \frac{m\pi x}{l}$ was found difficult to sum, so in the following calculations sufficient number of terms have been taken in order to get values correct to the second place of decimals. Taking $t = 1$ hour and $l = 10$ cms, a series of values have been calculated and are given in the following table. (Table VI.)

[1] Landolt, p. 1124.
[2] Compt. rend., **134**, 595 (1902).

TABLE VI

Distribution of concentration in the gel after 1/24 day (1 hour) taking l = 10 cms.

No.	x (cm)	Concentration of K_2CrO_4 N/150 solution used.)	Concentration of $AgNO_3$ (0.5M used) = N/2	Excess of $AgNO_3$ present	Excess of K_2CrO_4 present
1	.1	.0014 N	.356 N	.3566 N	—
2	.2	.00272 N	.2345 N	.23178 N	—
3	.25	.00335 N	.182 N	.1786 N	—
4	.4	.00497 N	.0735 N	.0685 N	—
5	.5	.00563 N	.035 N	.0294 N	—
6	.6	.00604 N	.015 N	.009 N	—
7	.75	.00652 N	.0035 N	—	.003 N
8	.85	.00659 N	.001 N	—	.0056 N
9	1.0	.0066 N	0.	—	.0066 N
10	1.25	.0066 N	0.	—	.0066 N

An Explanation of Liesegang Ring Formation

In the foregoing experiments it was found that two equivalent reacting solutions will give a precipitate only when forming a definite amount of silver chromate, the amount depending on the concentration of the gelatine solution used. The values obtained experimentally for different gelatine concentrations are given in Table VII:

TABLE VII

	Concentration of gelatine solution.	Amount of silver chromate formed at the first precipitation point.
1.	0.04%	0.009 gm in 20 ccs, i. e. 1/367 N.Ag_2CrO_4
2.	0.1%	0.01 gm in 20 ccs, i. e. 1/330 N.Ag_2CrO_4
3.	0.2%	0.0133 gm in 20 ccs, i. e. 1/248 N. "
4.	0.4%	0.0149 gm in 20 ccs, i. e. 1/222 N. "

The above amounts of silver chromate formed at the first coagulation points have been plotted against the gelatine concentrations in Fig. 6. From this curve the amount of silver chromate at the precipitation point for a 0.8% gelatine solution is found to be about 0.017 gram in 20 ccs i. e. 0.0052 N silver chromate.

Therefore in a 0.8% gelatine gel, one would expect the silver chromate to be a precipitate when the two reacting solutions are each about 0.0052 N. This condition is very nearly satisfied between 0.6 and 0.75 cms from the top of the gel as can be seen from Table VI. In Fig. 7, the concentrations of silver nitrate and potassium chromate have been plotted against distances of various layers of the gel, and it is found from the curve that at a distance of about 0.69 cms from the top the two solutions are equivalent, each being 0.006 N. Thus in this layer 0.006 N silver chromate would be formed. One

would therefore expect this layer to be a precipitate, because it has been shown by actual experiment that 0.0052 N silver chromate when formed in 0.8% gelatine is a precipitate.

From Fig. 7 we also find that 0.0025 N. silver chromate would be formed at a distance of about 0.175 cm from the top of the gel. From Table IV, however, we find that 0.0084 gram (i. e. 0.0025 N.) of silver chromate when formed in 0.8% gelatine comes down as a precipitate only in presence of 0.01 gram of silver nitrate, but is perfectly peptised in presence of larger quantities

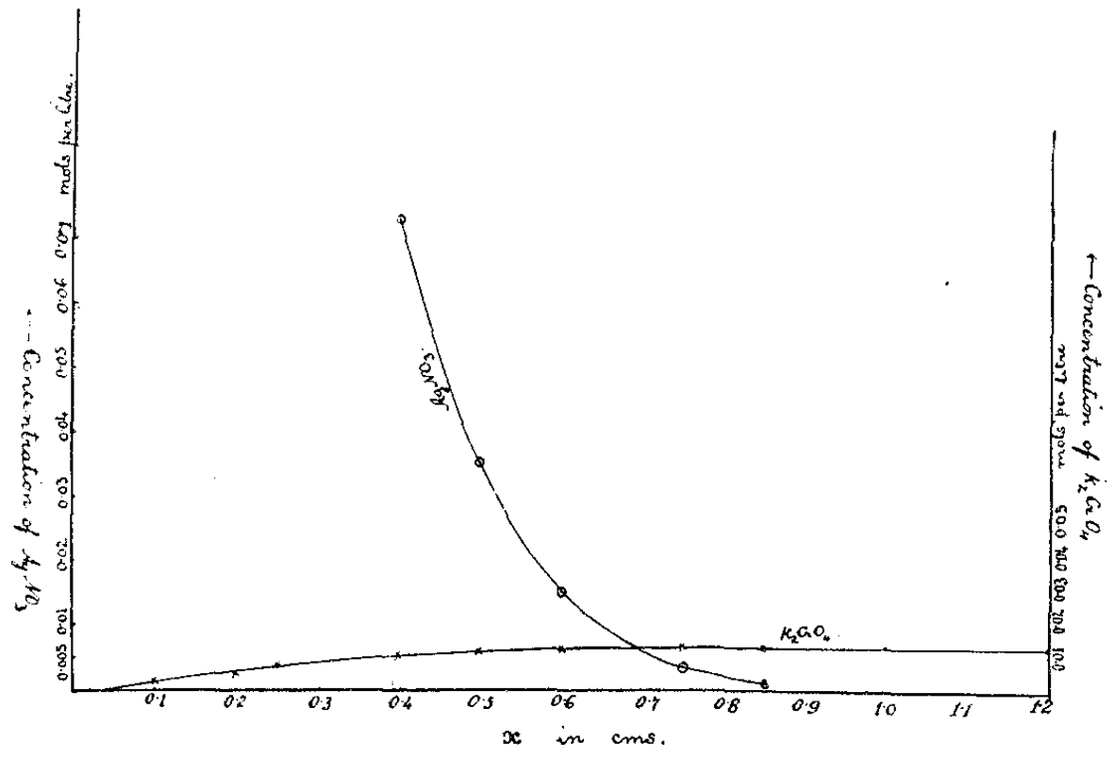


FIG. 7

of silver nitrate. From Table VI, we again find that there is a very large amount of silver nitrate present in that layer, in fact much larger than 0.01 gram per 20 ccs. Evidently then at that layer there will be a perfectly peptised sol. If we consider the layer of the gel say at 0.05 cm from the top, the amount of silver nitrate present in excess in that layer is enormously large, about 700 times the amount of potassium chromate. So one would expect precipitation in that layer.

From the above considerations, therefore, we clearly see that there will be layers of precipitate at distances of 0.05 and 0.7 cm from the top of the gel. There will also be a layer at a distance of 0.175 cm from the top of the gel in the neighbourhood of which, all the silver chromate will be in a stabilised or colloidal form. Other layers will be expected intermediately, near 0.4 cm from the top, depending on the particular concentration of silver nitrate that is capable of producing a precipitate with a certain concentration of silver chromate.

In the above calculations a static state of affairs has been assumed for a period of one hour. This assumption gets more and more justifiable as the

period decreases. There seems however every reason to suppose that there is no intrinsic change in the nature of the reaction, as the period, over which the diffusion process takes place, gets longer.

In an actual experiment, therefore, as the silver nitrate diffuses in, it meets a layer of potassium chromate and being itself in a very large concentration, forms a layer of precipitate. As it travels down in the gel, its concentration gets less and probably attains such a value that the amount of *silver nitrate present in excess, is the amount just wanted for the peptisation* of the amount of silver chromate formed in that layer. This layer is thus a peptised layer. Later on as the silver nitrate travels further in the gel, it, in all probability, meets the potassium chromate in equivalent concentration (or very nearly equivalent), and if the concentration has a certain value, the silver chromate formed in that layer comes down as a precipitate. It thus gives rise to a layer of precipitate. This process repeats itself as the silver nitrate diffuses onwards into the gel, and a series of alternately precipitated and peptised layers are thus obtained.

Summary

1. The stabilisation of silver chromate by gelatine and of lead chromate by agar-agar, have been studied. The above chromates were obtained by mixing solutions of the respective nitrates with a potassium chromate solution. The concentrations of the various reacting solutions, and of the stabilisers, were varied, one at a time, to study their respective influences on the stabilisation of the above mentioned substances.

2. By measuring their capacity, it has been possible to get a comparative measure of the extent to which the various resulting mixtures have been stabilised. For this purpose, the nephelometer devised by Kingslake, has been used with a slight modification.

3. To get reproducible results, it was found necessary to mix the above reacting solutions uniformly and simultaneously. An arrangement has been set up which meets the above purpose.

4. When gradually increasing amounts of silver chromate were formed, by the addition of a series of solutions of silver nitrate of gradually increasing concentrations, to a corresponding series of solutions of potassium chromate, the concentrations of each pair of the reacting solutions being exactly equivalent, it was found that the turbidities of the resulting mixtures varied in a periodic manner, although the amount of the stabiliser was constant throughout. There were two distinct zones at which the resulting mixtures showed the maximum turbidities.

5. The influence of the concentration of the stabilising solution, on these coagulation zones, has been studied. It was found that with increasing concentrations of the stabiliser, these zones become less and less prominent.

6. The influence of an excess of either Ag or CrO_4 ions on the stabilisation of silver chromate by gelatine has been studied quantitatively. It has been found that both the above ions have a distinct stabilising influence on silver chromate.

7. In the case of stabilisation of silver chromate by an excess of free Ag ions, a critical concentration was found; the Ag ions acted as a stabiliser, only when present in concentrations greater than this critical concentration. Free Ag ions, when present in concentrations below this critical value, had a distinct, though slight, coagulating influence.

8. The stabilisation of lead chromate by agar-agar has been studied. It has been found that the presence of an excess of free chromate ions greatly helps the peptisation of lead chromate by agar-agar, but lead ions do not seem to have any such effect.

9. It has been shown that lead chromate can adsorb chromate ions, but not lead ions. A colloidal solution of lead chromate has been prepared through the stabilising influence of chromate ions.

10. As a result of the foregoing experiments, it has been found that a solution of silver nitrate reacting with a potassium chromate solution, will form a turbid (precipitated) mixture, only when one of the following two conditions, is fulfilled:

(1) Unless very concentrated, if the two reacting solutions be equivalent, they will be precipitated only when the quantity of the silver chromate formed is a certain definite amount (which will be dependent on the concentration of the gelatine solution used). When the quantity of silver chromate is either greater or smaller than this amount a peptised solution will result.

(2) When one of the reacting solutions is used in excess, for a given weight of silver chromate, and a given gelatine concentration, precipitation will occur, only when a certain weight of one of the reacting substances is left in excess. If the amount of the substance left in excess, be greater or less than this quantity, a peptised sol instead of a precipitate will result.

11. The distribution of concentrations of a pair of silver nitrate and potassium chromate solutions of given concentrations, in a gelatine gel, has been calculated by using Fick's diffusion equation.

12. By correlating the values from the above calculations for the concentrations at different strata of the gelatine gel with the experimental observations, it has been shown that certain layers of the gel will contain Ag_2CrO_4 in a peptised form, whilst other layers will consist of precipitated silver chromate.

In conclusion the author wishes to express his thanks to Prof. Donnan, for his many valuable suggestions and for his kind interest in this work.

The William Ramsay Laboratories of Physical and Inorganic Chemistry,
University College, London.
October 20, 1926.

THE SYSTEM SODIUM SULPHATE-WATER: I. THE DENSITIES AND SPECIFIC VOLUMES OF AQUEOUS SOLUTIONS OF SODIUM SULPHATE BETWEEN 25 AND 40°, AND THE FICTIVE VOLUMES OF SODIUM SULPHATE IN SOLUTION

BY R. E. GIBSON

In a study of the effect of pressure on the equilibria between salts and their solutions a knowledge of the Fictive Volumes of the salts in solution is of the utmost importance. To determine the fictive volumes, that is to say the increase in volume which an infinitely large volume of the solution undergoes when one gram of the salt is added, it is necessary to know the specific volumes of solutions of the salt at various concentrations to as high a degree of accuracy as possible. Such data were not available in the case of sodium sulphate and it is the object of this paper to supply the need.

Experimental

The work was divided roughly into two parts.

First, the densities, and hence the specific volumes of solutions containing from 1 to 28 per cent of sodium sulphate were accurately determined at 25°. For solutions containing up to 21 per cent of Na_2SO_4 the density could be determined directly at that temperature but in the case of solutions of higher concentration the density was found at 30° and then converted to that at 25°.

Second, by means of a dilatometer the change in specific volume per degree between 25° and 40° was found for each solution. By combining these results it was possible to calculate the specific volume of any solution of sodium sulphate between 25 and 40°.

Density Determinations. The densities of the solutions were found by a pycnometer method. The pycnometers, thermostat tank, balance, and weights were those described by Hall,[1] and his technique and precautionary measures were observed throughout.

The temperature of the bath was checked frequently by a 10-junction copper-constantan thermel, one limb of which dipped into the thermostat near the pycnometer while the other was immersed in melting ice. The thermel was constructed by the author and was calibrated against the Standard 25-junction element of the Bureau of Standards with the kind assistance of Dr. W. P. White. The E. M. F. of the thermel was read with a Wolff potentiometer. The mean fluctuation of the bath was ±0.005°. The standard cell of the potentiometer was calibrated at the Bureau of Standards.

Sodium sulphate. J. T. Baker's C. P. Analyzed crystalline sodium sulphate decahydrate was used. It was recrystallized from water three times, care being taken each time to free the crystals from adhering solution by suction. The purified crystals were then kept in a vacuum desiccator over

[1] Ralph E. Hall: J. Wash. Acad. Sci., **14**, 167 (1924).

KOH until they were reduced to a fine anhydrous powder. Finally the powdered salt was heated in a platinum vessel to 400-°500° for six hours. The loss in weight of the Na_2SO_4 during this operation never exceeded 0.1 per cent.

Solutions. For each determination a fresh solution was prepared directly from salt and water. Here again Hall's method was used and at no time did any trouble arise from the formation of bubbles of air in the solution. When large amounts of the salt were required, however, the salt was weighed directly in the standard flask wherein the solution was prepared. This method proved more reliable than washing the salt into the flask from a separate weighing vessel.

Procedure. Before each experiment the pycnometers were washed out with a chromic acid solution and with distilled water and dried by a current of dried, filtered air. They were then immersed in distilled water, dried with a linen cloth, and suspended on the balance arms. After half an hour, when equilibrium was attained, the difference in weight was taken, double weighings being made in all cases. The constancy of the weight of the solution-pycnometer was comparable with the figures given in Hall's paper. The solution-pycnometer was then filled, immersed in the thermostat, adjusted and weighed as Hall describes. The weight of the solution was corrected for the temperature, pressure, and the humidity of the air in the balance case.

Experiments with pure water gave the volume of the solution-pycnometer and were performed at intervals throughout the work. The results are given in Table I. The volume of the pycnometer at 25° is 55.0365 milliliters and at 30.0° is 55.0448 milliliters.

TABLE I

Calibration of Pycnometer

Temperature	Number of experiment	Weight of water
25°	1	54.8758
	2	54.8758
	3	54.8759
	4	54.8752
	5	54.8751
	6	54.8756
	7	54.8760
25°	Average	54.8756
30°	8	54.8073
	9	54.8068
	10	54.8068
30°	Average	54.8069

In order to avoid any errors due to elastic hysteresis in the glass, the experiments at 25° were all completed before those at 30° were undertaken.

Dilatometer Experiments. The dilatometer, used in the determination of the coefficients of expansion of the different solutions is shown in Fig. 1. It

consisted of a bulb, A, some 50 cc in capacity, to which was sealed a graduated capillary tube, C, whose internal diameter was about 1 mm. Liquid was introduced into the dilatometer through C by withdrawing the air at B. The stopcock D, was very carefully selected and gave no leakage trouble whatsoever.

The whole was then immersed in a large enclosed bath holding about 5 liters of water which was stirred vigorously. The bath was provided with an electrical heater and a cooling coil. By means of a variable resistance in series with the heater the temperature of the bath could be held within 0.1° of any point for any length of time. The temperature of the bath was read with the thermel described above. The position of the meniscus in the capillary was read with a lens, correct to 0.1 mm of the scale.

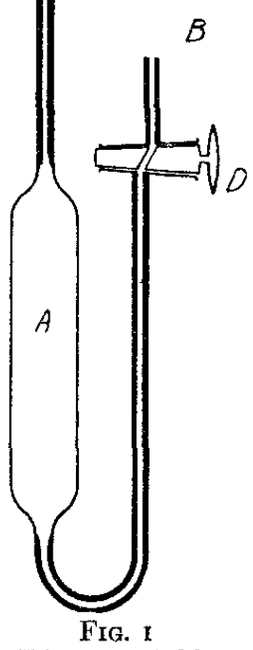


FIG. 1
Diagram of dilatometer

Procedure. After the dilatometer had been completely filled and was immersed in the bath at 25°, the stopcock, D, was opened and the liquid allowed to run very slowly down the capillary until the meniscus reached a certain definite zero mark. It was essential that the capillary should be absolutely clean and that no liquid should adhere to the upper portions of the capillary tube.

The stopcock was then closed and the whole was kept at 25° until equilibrium was attained, when the position of the meniscus was observed. The temperature was then raised slowly and readings were taken at intervals of 2.5°. In each case half an hour was allowed for the dilatometer to come into equilibrium with its surroundings. Owing to the limited length of the capillary the highest temperature reached was 37.5°, whereafter readings were taken with falling temperature down to 25°. If two readings at the same temperature differed by 0.2 mm., indicating hysteresis of the glass, leakage or formation of bubbles, the run was rejected. This was only necessary in one case.

A thermometer was suspended alongside the capillary and the air temperature was taken at the time of each reading. Hence a stem correction could be made to bring the volume of the liquid in the capillary to the volume it would occupy at the temperature of the bath.

Calibration of the dilatometer. The graduated capillary tube, C, was calibrated by means of a weighed thread of mercury. The bore was very regular indeed, the maximum and minimum cross section areas being 1.120 and 1.116 mm^2 respectively. The mean cross section area of the capillary was taken as 1.118 mm^2. The capillary was graduated in millimeters. The volume of the dilatometer at 25° was determined by weighing its water content at that temperature. It was 47.394 milliliters.

To determine the correction to be added for the expansion of the glass, i. e. to convert *apparent* to *real* expansion, several runs were made with pure water whose coefficient of expansion was taken from the Smithsonian tables.

Let $\Delta h''$ represent the observed rise of the water in the capillary for a temperature rise of $\Delta t°$ and letΔv represent the increase in volume of 1 gram of water for the same change of temperature. Then if M is the mass of water in the dilatometer, $M\Delta v$ is the real expansion.

Also if a is the area of the cross section of the capillary and $\Delta h'$ is the rise in the level of the water which should occur, were there no expansion of the glass,

$$M\Delta v/a = \Delta h'$$

The correction $(\Delta h' - \Delta h'')$, was found for various temperatures and the curve of $(\Delta h' - \Delta h'')$ against temperature was plotted. The curve was accurately represented by the equation

$$(\Delta h' - \Delta h'') = 1.28\ (t - 25) \qquad \text{(A)}$$

Results

The results of the density determinations made at 25 and 30° are given in Table II. The weighings are corrected to vacuum. In Table III the first steps in rounding off the results to even concentrations are given. All the densities are reduced to 25° and in column 2 the corrections necessary to bring the check determinations to the same percentage have been made. Here the experimental consistency may be studied.

TABLE II

Density of Na_2SO_4 solutions

Experimental results

Temp.	Weight of salt	Weight of solution	Concentration per cent (x_2)	Weight of solution in pycnometer	Density
25°	1.0002	102.6038	0.9748	55.3598	1.005875
	2.0005	101.7751	1.9656	55.8503	1.014787
	3.0016	102.9788	2.9148	56.3209	1.023338
	5.0029	104.7829	4.7746	57.2524	1.040263
	4.9999	104.7727	4.7721	57.2524	1.040263
	5.0070	104.9138	4.7725	57.2521	1.040257
	10.1053	108.5147	9.3124	59. 770	1.082500
	11.0037	109.7683	10.0245	59.5 97	1.089272
	11.0079	109.9376	10.0129	59.9443	1.089174
	12.9986	104.8549	12.3968	61.2096	1.112164
	15.8300	110.9914	14.2624	62.2206	1.130534
	23.0650	117.1804	19.6833	65.2576	1.185716
	25.0054	118.3059	21.1362	66.1004	1.201029
	25.0074	118.3573	21.1287	66.0955	1.200940
	25.0058	118.3467	21.1293	66.0965	1.200958
30°	30.0248	120.1801	24.9832	68.2497	1.239890
	35.2489	126.0318	27.9683	70.0807	1.273157

TABLE III

Densities of Na_2SO_4 solutions at 25°, all check determinations corrected to the same concentrations

x_2	Density	Final value	Calculated values Eqn. (1)	Obs-Calc $\times 10^6$	Calculated values Eqn. (2)	Obs-Calc $\times 10^6$
0.9748	1.005875	1.005875	1.005925	−50	1.005807	+68
1.9656	1.014787	1.014787	1.014726	+61	1.014725	+62
2.9148	1.023338	1.023338	1.023230	+108	1.023314	+24
4.7730	1.040249	1.040249	1.040083	+166	1.040267	−18
	1.040271					
	1.040261					
	1.040251*					
	1.040248*					
9.3124	1.082501	1.082501	1.082435	+66	1.082590	−89
10.0200	1.089232	1.089236	1.089187	+49	1.089319	−83
	1.089240					
12.3968	1.112164	1.112164	1.112186	−22	1.112218	−54
14.2624	1.130534	1.130534	1.130579	−45	1.130534	0
19.6833	1.185717	1.185717	1.185764	−47	1.185692	+25
21.1362	1.201029	1.201020	1.201010	+10	1.201020	0
	1.201012					
	1.201019					
24.9832	1.242568	1.242569	1.242326	+243	1.242844	−275
27.9685	1.275917	1.275917	1.275359	+558	1.276644	−727

*4th and 5th values were taken from work in which a larger pycnometer was used.

Empirical equations giving the relation between density and concentration in solutions. In order to find the values of the densities of solutions of even concentrations, as are given in Table IV, it was expedient to find a simple equation which would represent density as a function of concentration as accurately as possible. It is usual to employ a power series for this purpose and such may be derived from a difference table or by the solution of simultaneous equations, but the labor involved in the derivation of a cubic or biquadratic is very considerable.

Moreover, when differentiated, as is necessary in the computation of fictive volumes, these power series do not simplify at all. Hence another type of equation was sought.

It was found that the equation

$$\log \rho = ax_2 + b \qquad \text{(B)}$$

where ρ is the density, x_2 is the percentage of Na_2SO_4 and a and b are constants, fits the observations as well as a cubic equation. In Table III are the calculated values obtained from Equation 1, a logarithmic one, and Equation 2, a cubic one. In columns 5 and 7 the differences between the observed and calculated values are given. These differences, when plotted against the concentration, gave the deviation curves.

The equations from which the final calculations were made were:

Eqn. (1) $\log \rho = 0.00381823\, x_2 - 0.0011563$

Eqn. (2) $\rho = 0.997077 + 0.00893498\, x_2 + 0.00002094\, x_2^2 + 0.0000006075 x_2^3$

Eqn. (3) $\log \rho = 0.0038256\, x_2 - 0.0012570$

Equation 3 was derived for the range of concentration, 10 to 28 per cent, so that a check on the calculations at higher concentrations might be made. By combining each of these equations with the appropriate deviation curve we calculated the densities corresponding to even percentages of Na_2SO_4 and these are shown together in Table IV. In column 5 the mean of the three sets of values is given and a weighted mean is shown in column 6. When the difficulties of drawing an accurate deviation curve are considered, it will be seen that the agreement among the three interpolations is very satisfactory. The specific volumes of solutions of Na_2SO_4 at 25° are given in column 7.

TABLE IV

Final values of densities and specific volumes of solutions of Na_2SO_4

x_2	Density Eqn. (1)	Density Eqn. (2)	Density Eqn. (3)	Mean	Final values (Weighted mean)	Specific volumes
0					0.997077	
1.0	1.006104	1.006101		1.006102_2	1.006102_2	0.993935
2.0	1.015093	1.015096		1.015094	1.015094	0.985130
3.0	1.024115	1.024119		1.024117	1.024117	0.976451
5.0	1.042331	1.042329		1.042330	1.042330	0.959389
10.0	1.089044	1.089043	1.089043	1.089043	1.089043	0.918237
15.0	1.137878	1.137878	1.137880	1.137879	1.137878	0.878827
20.0	1.189036	1.189036	1.189039	1.189036	1.189036	0.841017
21.0	1.199573	1.199570	1.199572	1.199571	1.199570	0.833632
25.0	1.242754	1.242754	1.242754	1.242754	1.242754	0.804664
28.0	1.276276	1.276277	1.276271	1.276276	1.276276	0.783530
(29.0)	(1.287666)		(1.287663)	(1.287664)	(1.287664)	(0.776600)

Results of the Dilatometer Experiments

From experiments the following quantities were obtained directly:

R_0 = the height of the meniscus in the capillary at 25°.

R = height of the meniscus (corrected for stem temperature) at t°.

t = the temperature of the bath.

It was found most convenient to work with $\Delta t = t - 25$, so this quantity will be used throughout.

$R - R_0$ is a function of the apparent expansion and was converted to Δh, a function of the real expansion, by adding the appropriate correction from Equation A.

Then, if a be the cross section of the capillary, V_{25}, the volume of the dilatometer at 25° and $\Delta V/V_{25}$ the relative change in volume or the increase in volume which 1 cc (at 25°) of the solution undergoes when its temperature is raised Δt°,

$$\Delta V/V_{25} = a\Delta h/V_{25}.$$

TABLE V

Relative changes in volume of solutions of Na_2SO_4, $\Delta V/V_{25}$

0% Na_2SO_4				1% Na_2SO_4			5.30% Na_2SO_4			10.00% Na_2SO_4		
$10^3a' = 0.002$				$10^3a' = -0.002$			$10^3a' = -0.001$			$10^3a' = 0.001$		
$10^3b' = 0.2599$				$10^3b' = 0.2740$			$10^3b' = 0.3240$			$10^3b' = 0.3630$		
$10^3c' = 0.00435$				$10^3c' = 0.00420$			$10^3c' = 0.00330$			$10^3c' = 0.00259$		
	$\Delta V/V_{25} \times 10^3$		Diff.	$\Delta V/V_{25} \times 10^3$		Diff.	$\Delta V/V_{25} \times 10^3$		Diff.	$\Delta V/V_{25} \times 10^3$		Diff.
Temp.	(Obs)	(Calc)	$\times 10^5$	(Obs)	(Calc)	$\times 10^5$	(Obs)	(Calc)	$\times 10^5$	(Obs)	(Calc)	$\times 10^5$
25.0	0	−0.002	+2	0	−0.002	+2	0	−0.001	+1	0	+0.001	−1
27.5	0.673	+0.675	−2	0.709	0.709	0	0.829	0.830	−1	0.926	0.925	+1
30.0	1.405	1.406	−1	1.470	1.473	−3	1.701	1.702	−1	1.882	1.881	+1
32.5	2.194	2.192	+2	2.292	2.289	+3	2.615	2.615	0	2.867	2.869	−2
35.0	3.034	3.032	+2	3.162	3.158	+4	3.572	3.569	+3	3.890	3.890	0
37.5	3.925	3.926	−1	4.078	4.080	−2	4.564	4.565	−1	4.944	4.943	+1

14.81 %Na_2SO_4				19.81% Na_2SO_4			25% Na_2SO_4			28% Na_2SO_4		
$10^3a' = 0.000$				$10^3a' = 0.001$			$10^3a' = -0.001$			$10^3a' = -0.003$		
$10^3b' = 0.3929$				$10^3b' = 0.4126$			$10^3b' = 0.4256$			$10^3b' = 0.42967$		
$10^3c' = 0.00199$				$10^3c' = 0.00164$			$10^3c' = 0.00121$			$10^3c' = 0.00105$		
	$\Delta V/V_{25} \times 10^3$		Diff.	$\Delta V/V_{25} \times 10^3$		Diff.	$\Delta V/V_{25} \times 10^3$		Diff.	$\Delta V/V_{25} \times 10^3$		Diff.
Temp.	(obs)	(Calc)	$\times 10^5$	(Obs)	(Calc)	$\times 10^5$	(Obs)	(Calc)	$\times 10^5$	(Obs)	(Calc)	$\times 10^5$
25.0	0	0.000	0	0	0.001	−1	0	−0.001	+1	0	−0.003	+3
27.5	0.992	0.994	−2	1.044	1.043	+1	1.070	1.071	−1	1.075	1.077	−2
30.0	2.018	2.014	+4	2.104	2.105	−1	2.158	2.157	+1	2.168	2.171	−3
32.5	3.054	3.058	−4	3.183	3.187	−4	3.256	3.259	−3	3.282	3.279	+3
35.0	4.128	4.127	+1	4.294	4.290	+4	4.381	4.376	+5	4.404	3.399	+5
37.5	5.221	5.221	0	5.412	5.412	0	5.506	5.508	−2	5.530	5.532	−2

$\Delta V/V_{25}$ was used in all the intermediate steps as it is quite independent of the specific volume of the solutions at 25° and so the slight corrections to bring the observed results to those for even percentages of salt could readily be made by straight interpolation. For each solution observations were taken at six temperatures and quadratic equations were obtained to represent $\Delta V/V_{25}$ as a function of Δt by the method of least squares.

The equations were of the form

$$\Delta V/V_{25} = a' + b't + c't^2 \qquad \text{(C)}$$

In Table V the results on the relative changes of volume of solutions of Na_2SO_4 are given in a complete form. For each concentration the observed volume changes are shown and alongside them are written the volume changes calculated from the quadratic equation. The column marked "Diff." contains the difference between the observed and calculated values and demonstrates how closely the equations fit. The coefficients a', b', and c' are given at the head of each column.

The quantity sought, however, was Δv, the increase in the *specific* volume for a given rise of temperature, or the expansion per gram of solution.

TABLE VI

Calculation of coefficients b and c

x_2	$b' \times 10^3$	$c' \times 10^3$	v (at 25°)	$b \times 10^3$	$c \times 10^3$
0	0.2599	0.00435	1.00293	0.2607	0.00436
1	0.2740	0.00420	0.99394	0.2723	0.00417
5	0.3210	0.00335	0.95938	0.3080	0.00321
10	0.3630	0.00259	0.91824	0.3333	0.00238
15	0.3938	0.00197	0.87883	0.3461	0.00173
20	0.4131	0.00163	0.84102	0.3474	0.00137
25	0.4256	0.00121	0.80466	0.3425	0.00097
28	0.4279	0.00105	0.78353	0.3367	0.00082

TABLE VII

The values of Δv, the increments in volume to be added to the specific volume at 25° to obtain the specific volume at t°.

Concentration per cent	$10^3 \Delta v$			
	$t = 25°$	$t = 30°$	$t = 35°$	$t = 40°$
0	0	1.413	3.043	4.892
1.0	0	1.466	3.140	5.023
5.0	0	1.620	3.401	5.342
10.0	0	1.727	3.571	5.536
15.0	0	1.774	3.634	5.581
20.0	0	1.771	3.611	5.519
25.0	0	1.737	3.522	5.356
28.0	0	1.705	3.449	5.136

It is obvious that $\Delta v/v_{25} = \Delta V/V_{25}$, or $\Delta v = v_{25}\,\Delta V/V_{25}$, where v_{25} is the specific volume of the solution in question at 25°.

Hence if $\Delta v = a + bt + ct^2$ (D)

$$a = a'v_{25},\ b = b'v_{25},\ c = c'v_{25}.$$

The calculation of the coefficients, b and c, is given in Table VI. This enables us at once to compute the specific volume of any solution of Na_2SO_4 between 25° and 40°.

In Table VII are given the values of Δv, the amount to be added to the specific volume at 25° to obtain the specific volume at t°.

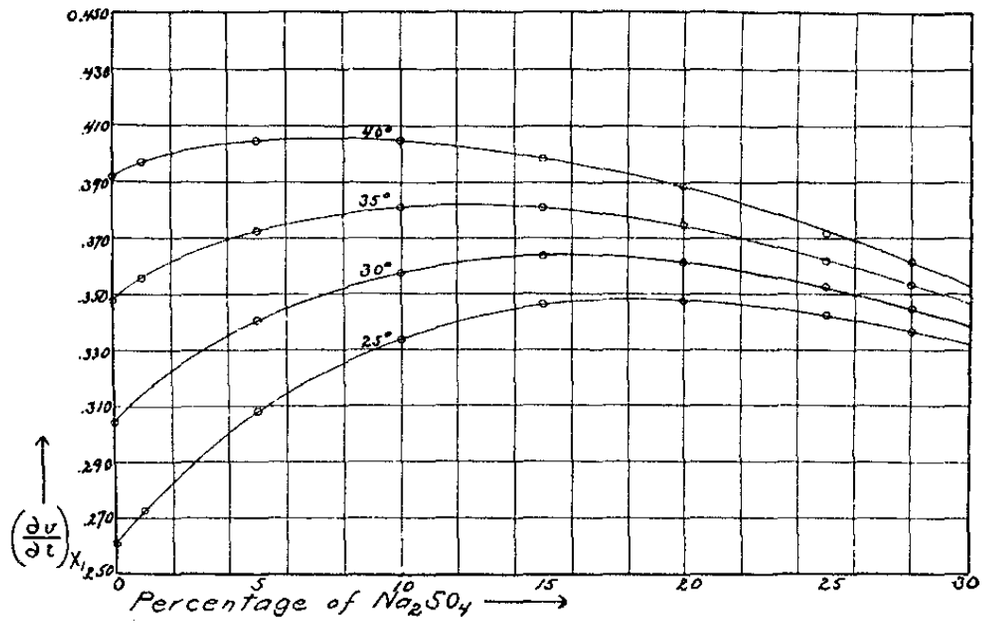


FIG. 2

The expansibilities of sodium sulphate solutions at various concentrations and temperatures.

By differentiating the equation (D)

$$v = a + bt + ct^2$$

we obtain $dv/dt = b + 2ct$ (E)

which is the coefficient of expansion of 1 gram of solution.

In Fig. 2 the values of $(b + 2ct)$ at 25, 30, 35, and 40° are plotted against the percentage of Na_2SO_4.

Calculations of the Fictive Volumes of Sodium Sulphate in Solution at 25°

Following the practice employed in the foregoing, we decided first to calculate the fictive volumes of the salt in solution at 25° and thereafter to derive the increments in fictive volume with temperature from the expansion equations.

Consider a system of two components, designated by the subscripts 1 and 2. Let m_1 and m_2 be the masses of the components present in a total volume V of the system. Then the fictive volume, v_1, of component (1) is given by the equation

$$v_1 = \left(\frac{\partial V}{\partial m_1}\right)_{m_2 p.T.}$$

If $x_1 = \frac{100\ m_1}{m_1+m_2}$ and $x_2 = \frac{100\ m_2}{m_1+m_2}$, the percentages of the components pre-

sent are used, it may easily be shown that

$$v_2 = x_1 \frac{dv}{dx_2} + v, \quad v_1 = x_2 \frac{dv}{dx_1} + v. \qquad \text{(F)}$$

where v is the specific volume of the system. In the present case we have considered Na_2SO_4 as component (2) and H_2O as component (1). It may be emphasized, however, that similar results would have been obtained had the components been $Na_2SO_4.nH_2O$ and H_2O.

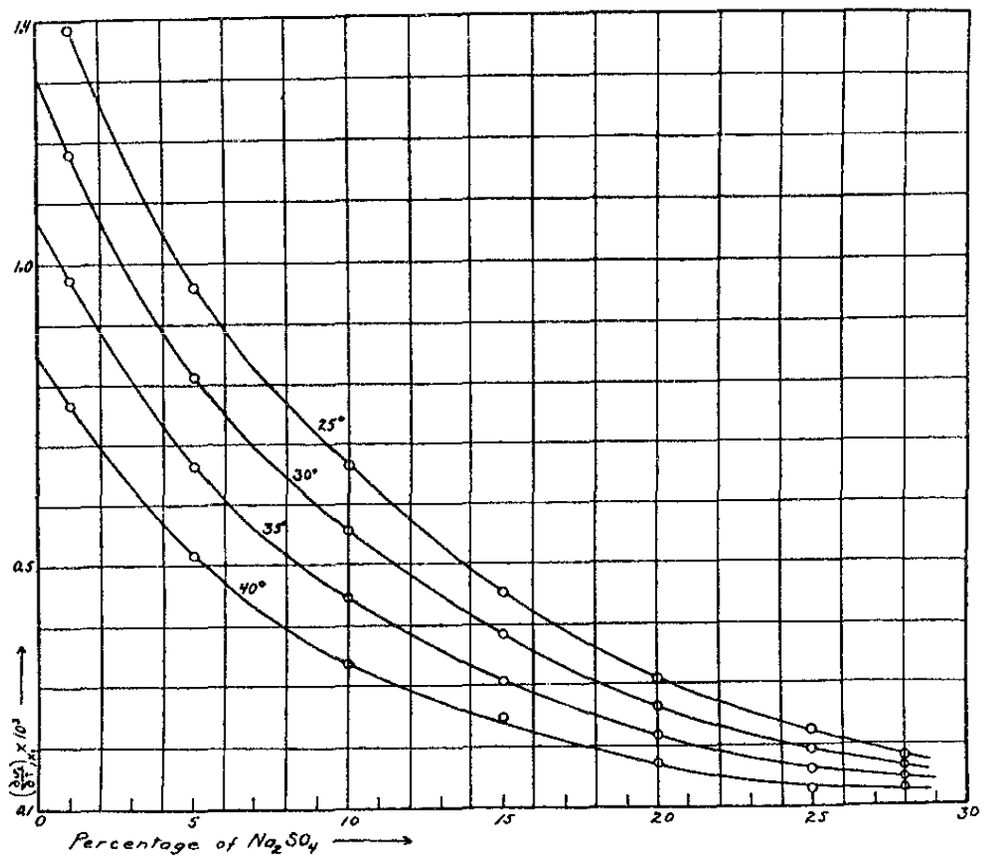


FIG. 3

The fictive expansibilities of sodium sulphate in solution at various concentrations and temperatures.

From the formula connecting density and concentration we have:

$$\log \rho = ax_2 + b$$

$$\text{i. e. } \log (1/v) = ax_2 + b$$

Hence $dv/dx_2 = -av \times 2.303$ (G)

Thus a first approximation to the fictive volume of a salt in solution may be given by the simple formula

$$v_2 = v\,(1 - 2.303\,ax_1) \qquad \text{(H)}$$

To obtain the highest accuracy from the observations, however, it is necessary to correct dv/dx_2 by a term from the deviation curve. From the deviation curves used for the interpolations described above a correction for $d\rho/dx_2$ was obtained graphically. This, on being multiplied by $-v^2$, gave the term to be added to $-av \times 2.303$ to obtain the best value of dv/dx_2.

In order to check the values obtained by this method the cubic equation was also differentiated and a corrected value of dv/dx_2 obtained with the aid of the deviation curve.

The results are given in Table VIII.

TABLE VIII

Fictive volumes of Na_2SO_4 in solution at 25°

x_2	v_2 (From Eqn. 4)	v_2 (From Eqn. 2)	v_2 (From Eqn. 3)	v_2 Final values (Weighted Mean)
0				(0.0860)
1.0	0.1140	0.1147		0.1144
2.0	0.1292	0.1287		0.1288
3.0	0.1392	0.1396		0.1394
5.0	0.1570	0.1581		0.1578
10.0	0.1942	0.1942	0.1937	0.1940
15.0	0.2223	0.2227	0.2227	0.2226
20.0	0.2476	0.2478	0.2479	0.2478
25.0	0.2699	0.2694	0.2702	0.2698
28.0	0.2826	0.2820	0.2827	0.2824
30.0				(0.2906)

In columns 2 and 4 are the values calculated with the help of Equations 1 and 3 and their deviation curves, while column 3 gives the figures from the cubic equation 2 and its deviation curve. The weighted mean is printed in column 5. The values in parentheses are the results of extrapolations using Equation K.

The fictive volumes at 25° are represented as a function of concentration with great exactness by the equation

$$\log (v_2 - 0.0860) = 0.58177 \log x_2 + \bar{2}.4518 \qquad (K)$$

The agreement between observed and calculated values is illustrated in Table IX.

TABLE IX

Comparison of the values of fictive volumes of Na_2SO_4 in solution at 25° with those calculated from Equation K.

x_2	v_2 (From observations)	v_2 (Calculated from Eqn. K)	Diff. $\times 10^4$
1.0	0.1144	0.1143	+1
2.0	0.1288	0.1284	+4
3.0	0.1394	0.1396	−2
5.0	0.1578	0.1582	−4
10.0	0.1940	0.1940	0
15.0	0.2226	0.2228	−2
20.0	0.2478	0.2477	+1
25.0	0.2698	0.2701	−3
28.0	0.2824	0.2826	−2

A glance at Equation K will show that 0.0860 = $(v_2)_0$, the fictive volume of the salt at zero concentration. Thus if we write $\Delta v_2 = [v_2 - (v_2)_0]$ we can convert the equation to the form

$$\Delta v_2 = 0.0283\ x_2^{0.58177} \qquad \text{(L)}$$

Although the specific volumes are given confidently to at least 1 part per 100,000, the fictive volumes calculated therefrom can only be written with an accuracy of 0.5 per cent. This is due to the fact that the slopes of the deviation curves influence the final values of the fictive volumes by about 5 per cent and in these deviation curve slopes the uncertainties arise. It should be emphasized that to obtain an accuracy of 1 to 0.1 per cent in the values of the fictive volumes, the specific volumes must be known to 0.001 per cent or closer.

Fictive Volumes and Fictive Expansibilities at Various Temperatures

The fictive volumes at 25° and the coefficients of expansion of the solutions having been obtained, it was a comparatively simple matter to pass to the fictive volumes at other temperatures.

If $(v_2)_{25}$ be the fictive volume at 25° and $(v)_{25}$ be the specific volume at that temperature,

then $(v)_t = (v)_{25} + bt + ct^2$, where b and c are the constants of Eqn. D.

Now $(v_2)_t = x_1 \mathrm{d}(v)_t/\mathrm{d}x_2 + (v)_t$

$= x_1\ \mathrm{d}/\mathrm{d}x_2\ [(v)_{25} + bt + ct^2] + (v)_{25} + bt + ct^2$

$= (v_2)_{25} + t\ (b + x_1 \mathrm{d}b/\mathrm{d}x_2) + t^2(c + x_1 \mathrm{d}c/\mathrm{d}x_2)$.

Or $(v_2)_t = (v_2)_{25} + Bt + Ct^2$ (M)

where $B = b + x_1 \mathrm{d}b/\mathrm{d}x_2$ and $C = c + x_1 \mathrm{d}c/\mathrm{d}x_2$.

The coefficients, B and C, are readily found from the slopes of the curves of b and c plotted against x_2 at 25°.

The values of the fictive volumes at 25, 30, 35, and 40° are given in Table X.

TABLE X

Fictive volumes of Na_2SO_4 in solution at different temperatures.

	Fictive volumes of Na_2SO_4			
x_2	$t = 25°$	$t = 30°$	$t = 35°$	$t = 40°$
0	0.0860			
1	0.1144	0.1208	0.1262	0.1306
5	0.1578	0.1622	0.1659	0.1689
10	0.1940	0.1970	0.1995	0.2015
15	0.2226	0.2247	0.2264	0.2279
20	0.2478	0.2492	0.2504	0.2514
25	0.2698	0.2708	0.2717	0.2724
28	0.2824	0.2833	0.2840	0.2847

By differentiation of Equation M with respect to temperature, keeping x_1 constant, we have $\left(\frac{\partial v_2}{\partial t}\right)_{x_2} = B + 2Ct$.

Hence α_2, the fictive expansibility of Na_2SO_4 in solution is given by

$$\alpha_2 = \left(\frac{\partial v_2}{\partial t}\right)_{x_2} = B + 2Ct.$$

In Fig. 3 the curves of α_2, as a function of x_2, are plotted for 25, 30, 35 and 40°

It may easily be shown that the fictive volume of the water, $\frac{\partial V}{\partial m_1} = v_1$, is given by the equation

$$v_1 = v - x_2 \, dv/dx_2$$

A mean of the three values of dv/dx_2 used for the calculations of the fictive volumes of the Na_2SO_4 was used for this computation of v_1 and the results are given in Table XI.

TABLE XI

Calculation of v_1 (fictive volume of H_2O in Na_2SO_4 solutions) at 25°

$$v_1 = v - x_2 \, dv/dx_2$$

x_2	$dv/dx_2 \times 10^2$	$x_2 \, dv/dx_2$	v	v_1
0			1.0029	1.0029
1	−.8884	−.0089	.9939	1.0028
2	−.8736	−.0175	.9851	1.0026
3	−.8630	−.0259	.9765	1.0025
5	−.8439	−.0422	.9594	1.0016
10	−.8045	−.0805	.9182	0.9987
15	−.7721	−.1158	.8788	0.9946
20	−.7416	−.1483	.8410	0.9893
25	−.7131	−.1783	.8047	0.9830
28	−.6958	−.1948	.7835	0.9783

Discussion of Results

The immediate purpose of this paper is the provision of thermodynamic data, so that very little discussion of the results will be attempted at this stage but attention may be drawn to the following points.

As would be expected, the specific volumes of the solutions and hence the fictive volumes show no sudden changes at 32.5°, the transition point of the decahydrate to the anhydrous salt. There are, however, strong indications that the salt is very highly hydrated in the dilute solutions at the lower temperatures and that as temperature and concentration increase this hydration gradually diminishes. We wish to use the term hydration, or in general, solvation, in a very broad sense and would define it as follows.

If a molecule or ion of a salt in a solution tends to alter its environment in such a way that the molecules of the solvent are more closely packed around the salt than in the pure solvent the salt is solvated in solution. In other words, if we introduce into water one molecule of a salt which is hydrated in solution, the molecule will hold to itself by attractive forces varying in intensity, n molecules of water.[1] The nature of the attracting forces and the magnitude of n are purposely left indefinite.

[1] A. Eucken: "Fundamentals of Physical Chemistry." (Translated by Jette and LaMer.) p. 245 (1925).

The first indications of a high degree of hydration of the sodium sulphate were found in the very low values of the fictive volume at low concentrations and the rapid rise in fictive volume with increase of concentration. Although the specific volume of Na_2SO_4 in the solid state is 0.375, the fictive volume at zero concentration is only 0.086 while the fictive volume in a 25 per cent solution is 0.27.

On the other hand, in the case of sodium chloride where the specific volume in the solid state is 0.462, the fictive volumes of the salt in solutions containing 0.5 and 25 per cent of NaCl are 0.30 and 0.40 respectively.[1]

Perhaps the most striking evidence of the apparent hydration of the salt in the solution is obtained from the curves for the fictive expansibilities in Fig. 3. In this diagram the fictive expansibilities of the Na_2SO_4, $\partial v_2/\partial t = \alpha_2$ are plotted against x_2 for four different temperatures. From the relative positions of the curves it will be seen that α_2 diminishes as the temperature is raised. Furthermore all the curves appear to converge on a value of α_2 which is of the order of 0.0001.

From the results of Jaeger[2] on the densities of molten salts we find that dv/dt for liquid Na_2SO_4 at 900° is 0.00023. This value is undoubtedly much higher than dv/dt for the undercooled liquid at 25°. In fact no large error would be made by supposing that at 25° dv/dt is of the order of 0.0001. We might, therefore, state with some degree of certainty that at higher temperatures and concentrations the fictive expansibility of Na_2SO_4 in solution tends to the value of the expansibility of the pure liquefied Na_2SO_4.

How are we to account for the very large values of the fictive expansibilities of Na_2SO_4 at the lower temperatures and concentrations? An explanation is forthcoming if we consider the fictive expansibility as the result of two factors: (1) the thermal expansion of the pure liquefied solute, and (2) the expansion due to the dissociation of the hydrate complexes as the temperature rises. If the salt is highly hydrated at the low temperatures and concentrations, then, as the temperature is raised, dehydration takes place and is made apparent through a large value of the fictive expansibility of the salt. As the solution becomes more concentrated, the salt is less hydrated and consequently the amount of dehydration per degree rise of temperature falls off and α_2 diminishes. Finally, when the concentration and temperature are high enough, we can assume that we are dealing with the almost anhydrous salt and a fairly constant value of α_2 is obtained.

In the above discussion we have assumed that factor (1) varies very slightly with dilution. Although this is at present not capable of proof, we can see from the flatness of the 40° curve that it is an approximation to the truth.

Thus it is the very rapid diminution in α_2 from its relatively large value at zero concentration and at 25° as temperature and concentration are increased which leads us to confirm the supposition that Na_2SO_4 is highly

[1] Unpublished calculations from the data on the densities of NaCl by Hall: op. cit.

[2] F. M. Jaeger: Z. anorg. allgem. Chem., **101**, 182 (1917).

hydrated in aqueous solution at low temperatures and concentrations and that this hydration decreases as temperature and concentration are increased.

The complex nature of water itself and the lack of further data prevent us from proceeding further with the discussion at present.

In conclusion the author wishes to take the opportunity of expressing his gratitude to Dr. L. H. Adams for his advice and criticism which have been frequently sought and freely given during the prosecution of the work.

Summary

The densities and specific volumes of solutions of sodium sulphate at 25° and over a range of concentration from 0 to 28 per cent have been determined with an accuracy of 5 to 10 parts per million. The thermal expansibilities have been determined for the same solutions between 25° and 40° with the same accuracy. From these data the fictive volumes of sodium sulphate and water in solutions of sodium sulphate have been calculated.

Geophysical Laboratory,
Carnegie Institution of Washington,
December, 1926.

AQUEOUS SOLUTIONS OF SODIUM SILICATES VI
HETEROGENEOUS EQUILIBRIA
SYSTEM: Na_2O:SiO_2:H_2O, AT 25°C

BY R. W. HARMAN

Introduction

There seems to be no doubt about the existence of the definite crystalline salt, sodium metasilicate, Na_2SiO_3. This series of investigations, comprising conductivity, transport numbers, hydroxyl ion concentration, sodium ion concentration, silicate ion concentration, and total osmotic activity measurements, on solutions of varying ratio Na_2O:SiO_2, indicates that Na_2SiO_3 exists as such in solution at 25°C and that in all probability a definite salt of the composition Na_2O:$2SiO_2$, the evidence already obtained pointing to $NaHSiO_3$, also exists in solution at this temperature,

Some indication of what salts do exist and are stable in solution, may be gained by means of a phase rule investigation of the ternary system Na_2O:-SiO_2:H_2O at 25°C. No such investigation is found in the literature; but some work, mostly from the Geophysical Laboratory, Washington, has been done in connection with the problem of alkali silicate melts at high temperatures.

Niggli,[1] by the hydrothermal quenching method, investigated the system R_2CO_3:SiO_2 (where R = Na, K, Li) in melts at temperatures ranging between 800°-1000°C. He concluded that the following equilibria existed:—

(1) $K_2CO_3 + K_2Si_2O_5 \rightleftarrows 2K_2SiO_3 + CO_2$
(2) $Na_2CO_3 + Na_2SiO_3 \rightleftarrows Na_4SiO_4 + CO_2$
(3) $2Li_2CO_3 + Li_4SiO_4 \rightleftarrows Li_8SiO_5 + 2CO_2$ (presumably)

In each system, the compound containing more silica is the poorest in silica which can be prepared pure, at the particular temperature, merely by melting together carbonate and SiO_2. Thus K_2SiO_3 or Na_4SiO_4 or Li_8SiO_5 cannot be prepared in the pure state from carbonate and silica at temperatures about 1000°C; the compounds $K_2Si_2O_5$, Na_2SiO_3, Li_4SiO_4 containing more silica can readily be obtained.

Both Niggli and Wallace[2] failed to obtain a definite salt richer in silica than the metasilicate. Morey[3] by the hydrothermal quenching method, investigated the system alkali silicate:water at temperatures 300°-400°C and higher. He obtained the following crystalline products:

(1) $K_2O.H_2O.4SiO_2$ or $KHSi_2O_5$, at 200°—450°C.
(2) $K_2O.2SiO_2$ or $K_2Si_2O_5$, at 500°C.
(3) $Na_2O.2SiO_2$ or $Na_2Si_2O_5$, above 400°C.
(4) $Na_2O.SiO_2$ or Na_2SiO_3, above 400°C.

[1] J. Am. Chem. Soc., **35**, 1693 (1913).
[2] Z. anorg. Chem., **63**, 1 (1909).
[3] J. Am. Chem. Soc., **36**, 215 (1914).

He observed that $KHSi_2O_5$ and $Na_2Si_2O_5$ were not readily affected by water, while $K_2Si_2O_5$ and Na_2SiO_3 were decomposed very rapidly. Morey's attempts to prepare the compound $NaHSi_2O_5$, analogous to $KHSi_2O_5$, were unsuccessful, as were also his efforts to obtain crystals of K_2SiO_3. In this connection it is interesting to note that Niggli found at higher temperatures in the systems $K_2O:SiO_2:CO_2$ and $Na_2O:SiO_2:CO_2$ that the stable alkali silicates were $K_2Si_2O_5$ and K_2SiO_3, and Na_2SiO_3 and Na_4SiO_4, increase in temperature in both cases favouring the second form. It seems therefore that in the soda system at lower temperatures $Na_2Si_2O_5$ is stable and that increase of temperature favours first Na_2SiO_3 and then presumably[1] Na_4SiO_4.

The ease with which the disilicates of sodium and potassium can be formed hydrothermally is in striking contrast to the rarity of the occurrence of minerals which can, with any degree of certainty, be considered essentially as disilicates i. e. as salts of the hypothetical acid $H_2Si_2O_5$. The only mineral that is unquestionably a disilicate is *rivaite* (Ca.Na) Si_2O_5, described by zambonini, and which occurs very sparingly among the ejected rocks at Vesuvius. Practically all the other minerals cited in the literature as disilicates contain alumina and may more rationally be regarded as derivatives of aluminosilicic acids.

It is most interesting to note that Morey did not obtain evidence of the existence of any of the many crystalline hydrates of Na_2SiO_3 described by previous workers.

Morey[2] has investigated the system $H_2O:K_2SiO_3:SiO_2$ at temperatures ranging from 200°-1000°C. He established the existence of:

(1) $KHSi_2O_5$ or $K_2O.H_2O.2SiO_2$, decomposed by H_2O below 420°C.

(2) $K_2Si_2O_5$ or $K_2O.2SiO_2$.

(3) $K_2Si_2O_5.H_2O$ or $K_2O.H_2O.2SiO_2$. rapidly decomposed by water at all temperatures.

(4) K_2SiO_3 or $K_2O.SiO_2$, the stable solid phase in the binary system $K_2SiO_3:H_2O$ from 010°-960°C, obtained in fairly pure condition by crystallising a metasilicate glass at high temperature.

(5) $K_2SiO_3.0.5H_2O$ or $K_2O.0.5H_2O.SiO_2$, stable from 370°-610°C.

(6) $K_2SiO_3.H_2O$ or $K_2O.H_2O.SiO_2$, decomposed by water at temperatures below 200°C.

In a later paper Morey[3] discusses the solubility and decomposition by water of glass and ceramic wares from the point of view of the phase rule, and brings out the distinction between compounds soluble in water and compounds decomposed by water, his observations being based on his already quoted work on the system $K_2SiO_3:SiO_2:H_2O$ at temperatures between 200°-1000°C. He concludes that K_2SiO_3 at 285°C has a true solubility in water represented by the endpoint of the saturation curve on the $K_2SiO_3:H_2O$ side of the diagram, but is decomposed by water at about 180°C, the actual solid phase be-

[1] Zambonini: Atti Accad. Sci. Napoli, **12**, No. 12, p. 16 (1912).

[2] J. Am. Chem. Soc., **39**, 1174 (1917).

[3] J. Soc. Glass Technology, **6**, 20 (1922).

ing $K_2SiO_3.H_2O$. From the fact that the tie-line H_2O:K_2SiO_3 cuts the saturation curve of $K_2SiO_3.H_2O$, it follows that this compound also has a true solubility in water at 285° C, but is decomposed by water at 200 °C. Morey did not follow the system to lower temperatures, but it is possible, from the general shape of all the stability fields, that at ordinary temperatures true equilibrium in any mixture of K_2O:SiO_2:H_2O would mean a solution containing a vanishingly small amount of SiO_2, the actual amount depending on the amount of K_2O present, in equilibrium with a solid crystalline phase of pure SiO_2 or a crystalline compound of SiO_2 and H_2O, if any such exists.

Morey and Bowen[1] studied the binary system Na_2SiO_3:SiO_2 in melts at temperatures round about 1000°C and obtained evidence of only two stable crystalline compounds.

(1) Na_2SiO_3 or $Na_2O.SiO_2$.
(2) $Na_2Si_2O_5$ or $Na_2O.2SiO_2$.

but found no solid solutions of SiO_2 in these salts as Wallace had suggested.

Thus a considerable amount of work has been done on the simple alkali silicate system, but all at high temperatures, ranging from 400°-1000°C, and by the hydrothermal quenching method, under which conditions Morey has established the stability of only two definite compounds, viz., $Na_2O.SiO_2$ and $Na_2O.2SiO_2$. From Niggli's work there seems a possibility also of the existence of $2Na_2O.SiO_2$ at high temperatures.

No work at all has been done in the wet way at ordinary temperatures, and so it was hoped that an investigation of the ternary system $Na_2O.H_2O$ at 25° C would indicate if any sodium silicates are stable in solution at this temperature, and what, if any, is the possible number and constitution of their hydrates.

Experimental

The method of residues was employed. The materials used were:

(1) Na_2SiO_3 prepared as described in Part I.[2]
(2) a powder of composition $Na_2O.2SiO_2$.
(3) a powder of composition $Na_2O.3SiO_2$.
(4) caustic soda.
(5) commercial solutions, of ratios varying from 1:2 to 1:5.

By using mixtures of the above materials it was possible to investigate nearly the whole system except that part towards the H_2O:SiO_2 side of the component triangle; but here another difficulty, probably insurmountable, arose, so that this part of the system is still incomplete. Nor does it seem possible to complete it at present, as will be shown later.

The mixtures of solid and water, or solution, were stirred vigorously in hard glass vessels immersed in a water thermostat kept at 25°C. The stirrer was fixed in through a mercury seal to exclude the CO_2 of the atmosphere, which at this temperature has a considerable effect on the equilibrium. It is unlikely that the mixtures have much effect on the glass vessel used, at this low

[1] J. Phys. Chem., **28**, 1167 (1924).
[2] J. Phys. Chem., **29**, 1155 (1925).

temperature. Even so, the effect would be merely to increase the alkali and silica, the other components of the glass introducing merely a negligible impurity. However, no noticeable effect on the glass vessels used was observed.

The mixtures were stirred continuously for over a week, in most cases from 8-14 days, depending on their viscosity, after which time the solution and the wet residues were analysed by the method already described in the paper on transport numbers.

The first difficulty encountered was that of obtaining some of the solution free from residue on account of its great viscosity.

Solutions of Na_2SiO_3, and mixtures of Na_2SiO_3, NaOH and H_2O were quite viscous, but not too viscous to be filtered so that a little of the clear solution could be obtained by filtering with the water pump. But in that part of the system lying between Na_2SiO_3:H_2O and the H_2O:SiO_2 side of the triangle, with increasing amounts of SiO_2 the viscosity became so great that all filtering methods were quite impossible. These very viscous solutions were allowed to stand in the thermostat after stirring continuosly for nearly two weeks, and then the clearest portion, in most cases the top, but in some cases the bottom part, was centrifuged for a couple of days. In this way a solution almost clear but still a little cloudy, was obtained for analysis. Of course, the obtaining of the wet residue for analysis gave no difficulty. Still not much residue was obtainable in these viscous solutions, because, if too much solid remained undissolved, the whole formed a plastic mass like putty; therefore the amounts were so chosen as to leave some residue but not too much, and this being wet with the very viscous solution, often brought the two points closer together on the diagram than is desirable for accuracy.

By this means the system was investigated between the ratios Na_2O:SiO_2 1:1 to 1:3, but it was felt that towards the ratio 1:3 the method was getting very doubtful. When solutions beyond the ratio 1:3 were attempted a new difficulty was encountered besides the viscosity. This was the fact that such an extremely viscous solution, when left to stand after stirring, set to what presumably was a gel. In fact, the mixture had most of the properties of silica gel—it was not sticky as all the other solutions were; it could be moulded into a ball, which was elastic, but which when placed on the bench slowly spread out. This not only made further experiments impracticable on this part of the system, but also cast doubt on the validity of the application of this method of investigation. This will be discussed later.

Results

The results are given in Table I. The method of analysis outlined in the paper on transport numbers[1] was closely followed.

[1] Harman: J. Phys. Chem., **30**, 359 (1926).

TABLE I

Analyses of Solutions and Residues

Solution			Residue		
Na_2O	SiO_2	H_2O	Na_2O	SiO_2	H_2O
0.37	8.74	81.89	10.51	9.94	79.55
0.45	2.22	88.33	12.48	6.75	80.77
13.70	1.19	85.11	14.50	3.46	82.04
24.48	1.34	74.18	24.02	5.48	70.50
27.52	1.84	70.64	27.25	7.52	65.23
29.58	1.90	68.51	29.74	5.04	65.22
33.02	2.92	64.06	31.96	7.57	60.47
35.54	2.94	61.52	35.70	10.06	54.24
36.39	0.49	63.12	36.75	7.75	55.50
44.78	0.85	54.37	45.31	5.82	48.87
14.11	19.65	66.25	16.20	20.26	65.54
19.32	31.33	49.35	20.18	27.71	52.11
16.57	31.30	52.23	17.72	35.44	46.84
10.53	28.80	60.67	11.19	29.95	58.86
36.75	11.65	51.60	36.07	14.90	49.03
		Theoretically Calculated			
21.80	21.21	56.99	$Na_2SiO_3.9H_2O$		
26.93	26.18	46.89	$Na_2SiO_3.6H_2O$		
37.06	36.04	26.89	$Na_2SiO_3.2.5H_2O$		
50.69	49.31	——	Na_2SiO_3		
17.99	34.98	47.00	$Na_2O.2SiO_2.9H_2O$		
53.45	——	46.55	$NaOH.1H_2O$		

Discussion of Results

It can be seen from Fig. 1 that there are only two types of solid phase:
(1) Na_2SiO_3 and its hydrates
(2) $Na_2O.2SiO_2.9H_2O$.

There is certainly at 25° C no compound richer in silica than the metasilicate. Both Jordis and Vesterberg (see below) made experiments with silicate solutions containing a great excess of alkali, as much as 14 $Na_2O.SiO_2$, but obtained no crystals richer in alkali than the metasilicate. Also, in view of the very colloidal nature of the mixtures obtained in this investigation above ratio 1:3, there is almost certainly no salt richer in silica than $Na_2O.SiO_2$.

Considering first the metasilicate and its hydrates we have:—

(1) Na_2SiO_3 anhydrous, enclosed by the saturation curve GH and the tie-lines from GH converging on D, on the Na_2O-SiO_2 side of the component triangle.

(2) $Na_2SiO_3.2.5H_2O$, enclosed by the saturation curve HI and the tie-lines converging on C, the point C representing almost exactly $Na_2O.SiO_2.2.5H_2O$.

(3) $Na_2SiO_3.6H_2O$, defined by the curve IJ and the point B.

(4) $Na_2SiO_3.9H_2O$, enclosed by the saturation curve JKL and the tie-lines converging on A. The tie-line from A to the H_2O apex cuts this saturation curve of $Na_2SiO_3.9H_2O$ and so this hydrate is stable in solution, i. e. has a true solubility in water.

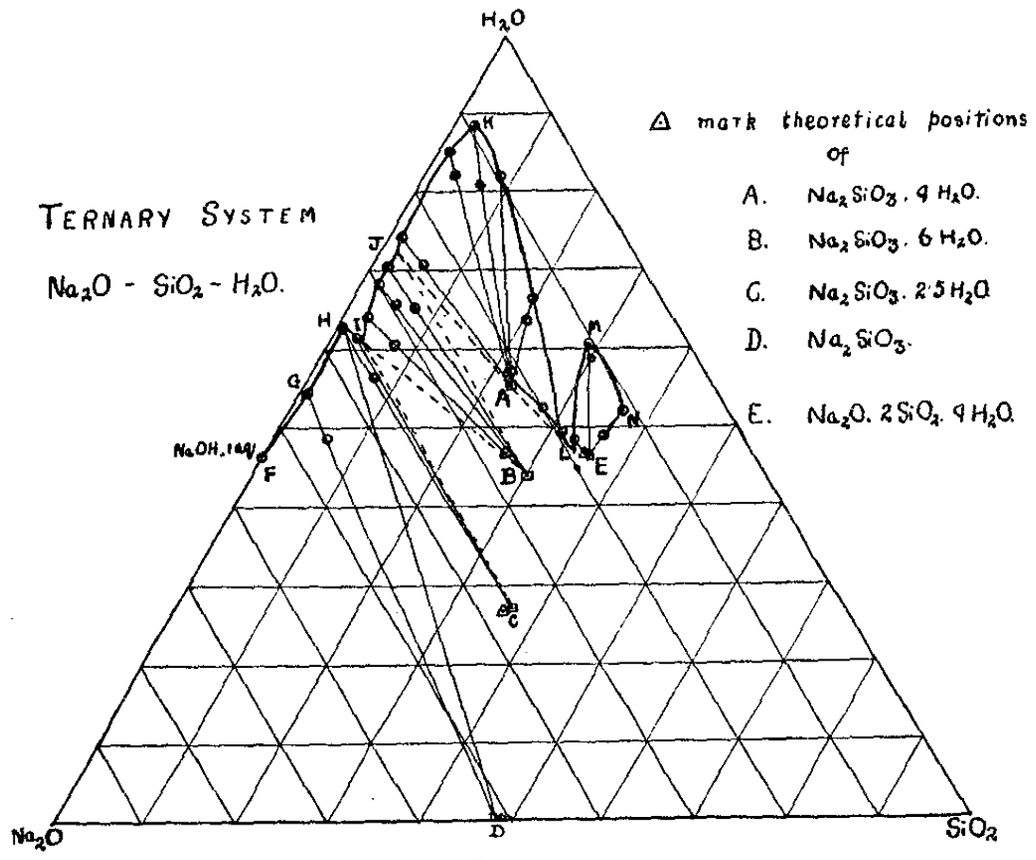


FIG. 1

The tie-lines from B and C to the water apex do not cut the saturation curves of $Na_2SiO_3.6H_2O$ and $Na_2SiO_3.2.5H_2O$, hence these hydrates are decomposed by water. Therefore the only hydrate expected to crystallise from solution of ratio 1:1 would be the nona-hydrate, and this has actually been found true in the present invesiigation. Large well-defined crystals of $Na_2SiO_3.9H_2O$ have also been obtained from a solution of ratio 2:1 and concentration 2 N_w, without the addition of alcohol or without seeding. The other two hydrates are stable in more alkaline solution and may be prepared therefrom.[1]

In connection with these hydrates there is rather a volumnious literature, as many authors have described crystals of sodium metasilicate, obtained from aqueous and alcoholic alkaline silicate solutions at ordinary temperatures, but the observations recorded are not at all concordant. Thus Petersen[2] described a monoclinic crystalline $Na_2SiO_3.6H_2O$; Fritsche[3] described in detail triclinic crystals containing $6H_2O$; Yorke[4] reports 7 aq.; severalobservers

[1] See Erdenbrecher: Z. anorg. Chem., **124**, 339 (1922).
[2] Ber., **5**, 409 (1872).
[3] Pogg. Ann., **43**, 135 (1838).
[4] Phil. Trans., **147**, 533 (1857).

have reported 8aq., including von Ammon[1] who described the monoclinic crystals he obtained; Jordis[2] found 6, 7, 8, 9, 10, 11, 12 H_2O; Vesterberg[3] found 9 aq. and from dehydration experiments concluded that hydrates containing 6 and 3 aq. respectively also exist; Erdenbrecher[4] obtained hydrates 9, 6 and 4 aq. respectively by crystallisation from an alkaline solution, increasing amounts of Na_2O in the ratio giving the lower hydrates; Morey[5] in his investigations at high temperatures found none of these hydrates. This question of the hydrates can now be considered definitely settled, i. e. there are three hydrates, containing 9, 6 and 2.5 H_2O respectively.

The saturation curve from L onwards cannot be said to have the same definite accuracy as from F to L, on account of the experimental difficulties encountered. However, it is definite enough to indicate that there is a compound $Na_2O.2SiO_2.9H_2O$ bounded by the curve LMN and the tie-lines converging on E.

A compound corresponding to this formula has not yet been obtained from solutions at ordinary temperatures, though Morey has attained the separation of crystalline $Na_2O.2SiO_2$ from solution at 400°C and from melts at about 1000°C. Also, much evidence from conductivity, transport numbers, hydroxyl and sodium ion concentration measurements, already described, may be adduced to show the existence of a compound of the formula $Na_2O.2SiO_2$ in solution at ordinary temperatures.

A number of investigators have obtained products containing 2 to 4 or more molecules of SiO_2 to one molecule of alkali oxide, but the preparative methods used are, in every case open to question, and the products were always amorphous. Most of these methods fall into two classes:—

(1) precipitation with alcohol

(2) determination of the ratio, alkali oxide to silica, in the saturated solution.

By the first method Forchhammer[6] obtained $Na_2O.3SiO_2$, but Ordway[7] has shown that this method leads to wholly erroneous results, because the composition of the precipitate depends on the concentration of the solution, the proportion of alkali present, and the amount of alcohol added, and varies continually with variation of any of the above factors. The second way is obviously wrong.

More recently Schwarz and Menner[8] claim to have obtained definite crystalline compounds of compositions corresponding to $Na_2O.SiO_2$; $Na_2O.-{}_2SiO_2$; $Na_2O.{}_3SiO_2$ by fusing pure quartz with Na_2CO_3 at 1150 C. They obtained $Na_2O.{}_2SiO_2$ and $Na_2O.3SiO_2$ as glasses which they state, transformed into definite compounds by heating at 700°C, for from 50-100 hours. Morey,

[1] Inaug. Diss. Göttingen (1862).
[2] Z. anorg. Chem., **56**, 305 (1907).
[3] Eighth Internat. Congress Applied Chemistry, **2**, 235 (1912).
[4] Z. anorg. Chem., **120**, 339 (1922).
[5] Loc. cit.
[6] Pogg. Ann., **35**, 343 (1835).
[7] Am. J. Sci., (2) **33**, 27 (1862).
[8] Ber., **57** B, 1477 (1924); **58** B, 73 (1925).

by his hydrothermal quenching method, obtained $Na_2O.2SiO_2$ but not $Na_2O.3SiO_2$.

Schwarz and Menner do not state that they examined these crystalline silicates microscopically, nor do they give any measurements of angles as Morey does.

It was found impossible to investigate the system beyond the point N, not only because of the extreme viscosity of the solutions, but also of the more serious obstacle due to mass setting to what was presumably a gel.

The fact that some or most of the silica in this region exists as colloidal silica renders the application of the phase rule invalid. If a sodium silicate dissolves in water with the formation of colloidal silica, the process will certainly go on until some more or less definite end point is reached; but this presumed equilibrium is in no way determined by the real solubility of sodium silicate itself. This objection cannot be raised against that part of the system represented by the region lying between $Na_2O.SiO_2$ and the H_2O: Na_2O side of the component triangle, as all the previous work described herein points to the fact that the metasilicate, is certainly not colloidal in solution. It also seems probable from the previous work by the author that there is no colloidal, matter, or at most, very little, in solution in the region up to 1:2. The fact that the tie-line from E to the H_2O apex cuts the saturation curve of $Na_2O.2SiO_2.9H_2O$ shows that this compound has a true solubility in water at this temperature. In spite of the colloidal nature of the region beyond N to the H_2O:SiO_2 side of the component triangle, we are quite justified in concluding that a compound $Na_2O.2SiO_2$ does exist in solution.

Summary

(1) Previous work in this field has been surveyed and summarised.

(2) An investigation of the ternary system Na_2O:SiO_2: H_2O at 25°C has been carried out and the results shown graphically.

(3) Towards the H_2O:SiO_2 side of the system the solutions became colloidal and so invalidated further work.

(4) Two compounds only are indicated as stable in solution,—$Na_2O.SiO_2$ and $Na_2O.2SiO_2$.

(5) Na_2SiO_3 crystallises with 9, 6 and 2.5 H_2O; $Na_2O.2SiO_2$ with $9H_2O$.

I wish to thank the Commissioners of the 1851 Exhibition Scholarship which has enabled me to carry out this investigation, and to express my gratitude to Professor Donnan, at whose suggestion this work was undertaken, for his constant kindly interest and advice.

The Sir William Ramsay Laboratories of Physical and Inorganic Chemistry,
University College, London.

October 14, 1926.

THE APPLICATION OF THE ELECTRON TUBE TO POTENTIOMETRIC TITRATIONS*

BY JOHN WARREN WILLIAMS AND THEODORE A. WHITENACK

The introduction of the electron or vacuum tube has made possible many accurate measurements in the field of chemistry as well as in physics. It is, of course, the familiar instrument used as both detector and amplifier in modern radio-communication, and need not be described here.

Thus far, there has been no extensive application of the electron tube to potentiometric titrations.[1] There is, however, every reason to believe that the application should be extensive, since the tube may be caused to function essentially as a potentiometer which draws virtually no current from the titration cell, neither can any current be supplied to the cell through the tube under proper working conditions.

Goode[2] was the first to apply the electron tube to a potentiometric titration. He showed "that the three-electrode vacuum valve ("audion") presents almost the ideal case of a "voltmeter" which draws no current from the source to be measured, and can therefore be employed as a continuous-reading instrument for determining the concentration of the hydrogen ion". In the second paper this investigator has described "an improved, continuous-reading hydrogen-ion meter" which makes "use of the three-electrode vacuum tube as a voltmeter, and 'as a direct current amplifier". The statement is made that the device serves to indicate the potential between any two electrodes ordinarily used in electro-chemical work; but the article, as its title indicates, intends the description of an apparatus for the determination of hydrogen ions.

Calhane and Cushing[3] applied an arrangement similar to that of Goode to the accurate titration of dilute sodium chloride solutions with silver nitrate. Treadwell[4], making use of a similar apparatus, has studied this same precipitation reaction. His arrangement differs from that of the previous investigators in that a potential (1.6 volts) has been introduced into the circuit in series between the negative or indicator electrode of the titration cell, and the grid of the electron tube.

The purpose of this paper is to show that the electron tube may be applied not only to the determination of hydrogen ion concentration and of the end point of certain precipitation reactions but to potentiometric titrations in general, at least to those which may be followed with analytical accuracy by the potentiometric method. This has been accomplished by a study of certain chemical reactions of the various types which have already been submitted to detailed investigation by the potentiometric method.

* Contribution from the Laboratory of Physical Chemistry, University of Wisconsin.

[1] Kolthoff and Furman: "Potentiometric Titrations", p. 159 (1926).

[2] Goode: J. Am. Chem. Soc., **44**, 26 (1922); **47**, 2483 (1925).

[3] Calhane and Cushing: J. Ind. Eng. Chem. **15**, 1118, (1923).

[4] Treadwell: Helv. Chim. Acta, **8**, 89 (1925).

Method

The method used is similar in principle to that of Goode, Calhane and Cushing, and Treadwell. The electrode whose potential indicates the change in concentration of the ion to be titrated is called the indicator electrode. Its potential may be determined by means of another electrode which has a constant potential, the two electrodes giving an electromotive force which can be measured. The change in this electromotive force during a potentiometric titration is then equal to the change of potential of the indicator electrode. At the equivalence point of the titration the rate of change of this

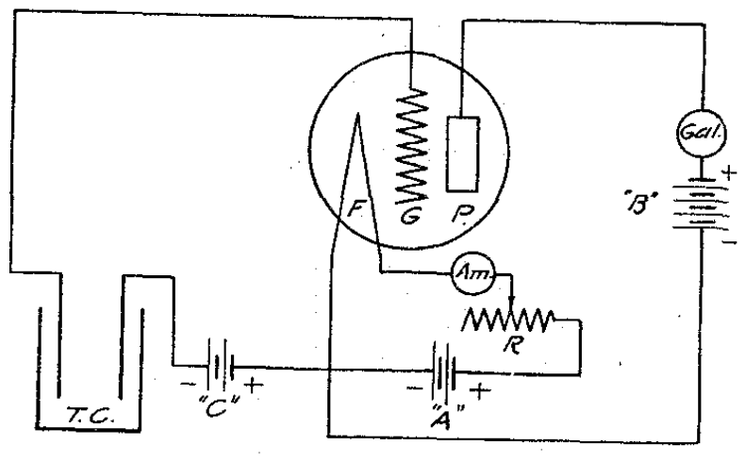


FIG. 1

potential with a small change in concentration assumes a maximum value. If now, the potential of the indicator electrode be impressed upon the grid element of an electron tube the value of the plate current will be regulated by the change of potential of the electrode. The plate current may be measured by an ordinary wall galvanometer with a suitable shunt. The equivalence point is indicated by the position of the break in the curve obtained by plotting cubic centimeters of titrating solution added as abscissae against galvanometer deflections as ordinates.

Apparatus

A diagram of the apparatus used is shown in Fig. 1. The vacuum tube was a Cunningham amplifier and detector, CX-299, whose filament operates normally at 3 volts, drawing 0.06 ampere. In the experiments to be described it was found most satisfactory to operate the tube at 0.04 ampere. The source of current, the "A" battery in the diagram, was an ordinary lead storage cell connected to the filament through a rheostat, R, and an ammeter, Am, by means of which the filament current was kept constant. The plate, or "B" battery consisted of several 22.5 volt units, any number of which could be used for best operation of the tube. The characteristics of the tube and galvanometer were such that normally 22.5 volts were used. The indicator electrode of the titration cell, T.C., was connected directly to the grid element of the tube and the calomel or reference electrode was connected through a battery, "C", of one or two dry cells, to the negative of the filament.

Experimental Procedure

The procedure may be illustrated by the description of a typical experiment in which a definite volume of a n/10 solution of ferrous ammonium sulfate was oxidized by a n/10 solution of potassium dichromate in acid solution. The apparatus was connected as above, the indicator electrode being simply a bright platinum wire. When the filament current was constant at 0.04 ampere a galvanometer shunt was adjusted so that a deflection of exactly 25

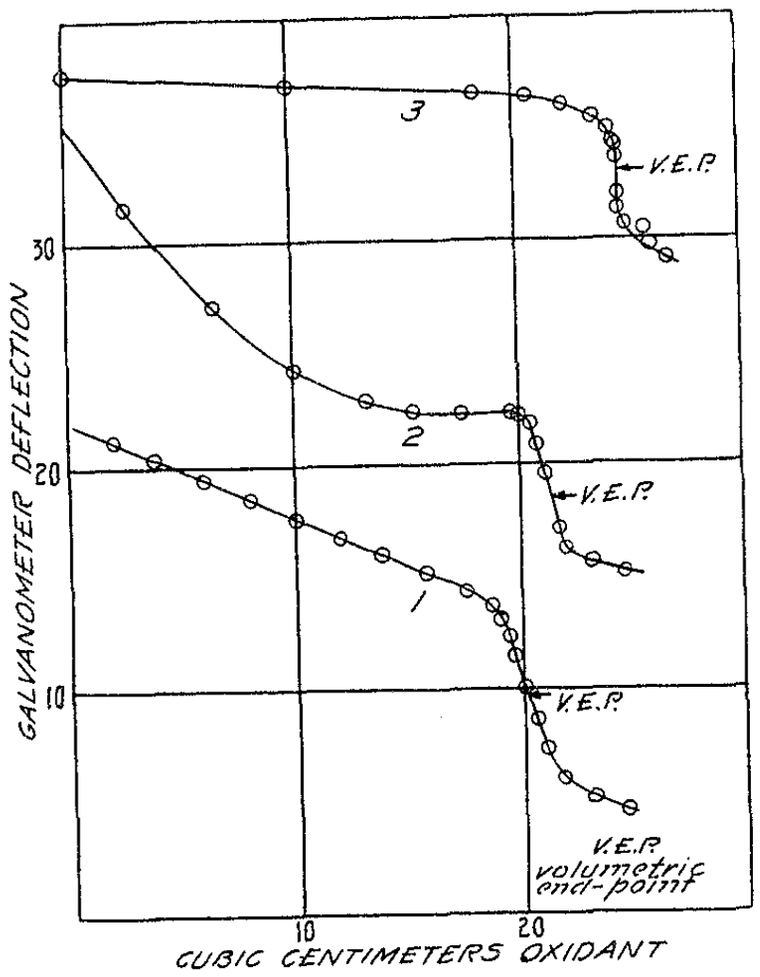


FIG. 2

Oxidation–Reduction Reactions

1. $HCrO_4' + 7H^+ + 3\,Fe^{++} \longrightarrow Cr^{\cdots} + 4\,H_2O + 3\,Fe^{\cdots}$
2. $2\,MnO_4' + 2H_2O + 3\,Mn^{++} \longrightarrow 5\,MnO_2 + 4\,H^{\cdot}$
3. $I_2 + 2S_2O_3'' \longrightarrow S_4O_6'' + 2I'$

centimeters on the scale was obtained. The potassium dichromate was titrated into the ferrous ammonium sulfate solution. At first, several cubic centimeters were added at a time, but, as the equivalence point was approached, readings of the galvanometer were taken more and more frequently. As the titration continued the potential of the indicator electrode became slightly more negative until the equivalence point was reached and the "break" came. This increasingly negative potential caused the plate current, and therefore the galvanometer deflection, to be decreased. The result of the titration was obtained from a curve, where the abscissae represent cubic

centimeters of titrating solution and the ordinates represent the corresponding galvanometer deflections. It is usually assumed that the inflection point indicates the equivalence point precisely, although in certain systems, especially in the case of oxidation-reduction reactions, the equivalence point is known to be somewhat beyond this point.[1]

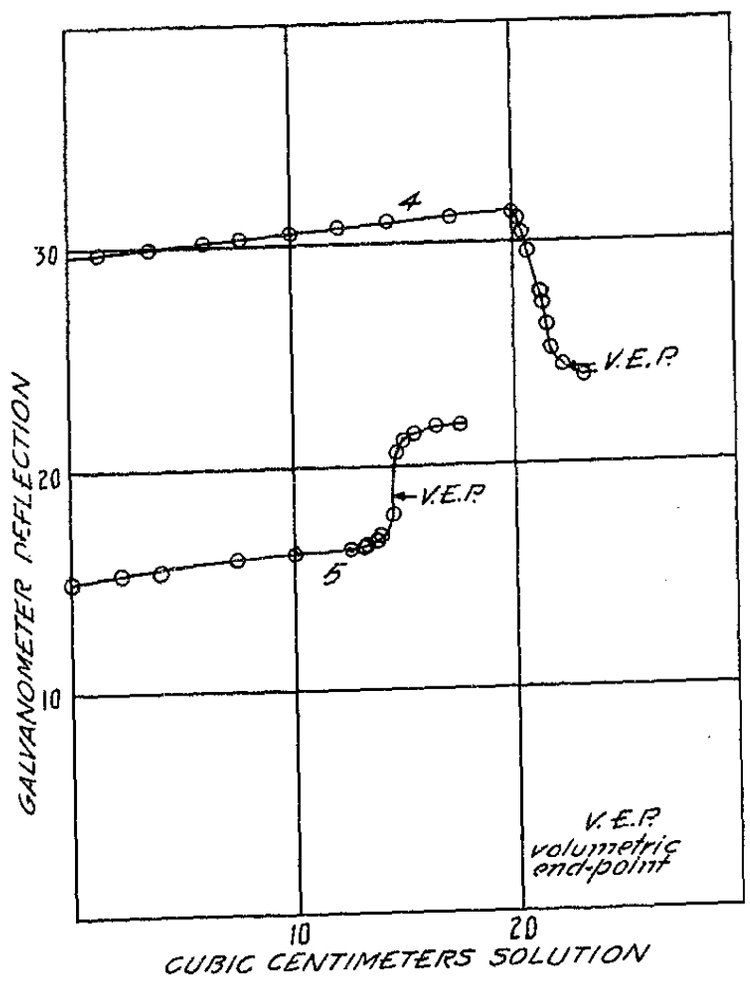


FIG. 3

Miscellaneous Reactions

4. Precipitation: $3Zn^{\cdot\cdot} + 2K_4Fe(CN)_6 \longrightarrow Zn_3K_2[Fe(CN)_6]_2$
5. Neutralization: $H^{\cdot} + OH' \longrightarrow H_2O$(HAc + KOH)

Experimental Results

Typical experimental results are shown in the accompanying graphs (Figs. 2 and 3) where galvanometer deflections are plotted against cubic centimeters of titrating solution added. The systems studied were chosen at random from the classification of reactions which give accurate end-points by the potentiometric method given in chapter "Electrometric Methods in Chemistry" of Taylor's "Treatise on Physical Chemistry".[2] On the basis of this classification three oxidation-reduction reactions[3] (shown in Fig. 2) and

[1] Kolthoff and Furman: "Potentiometric Titrations", Chaps. V and VI (1926).

[2] Taylor: "Treatise on Physical Chemistry", pp. 851-854 (1924).

[3] We are indebted to Mr. Penrose S. Albright for the experimental work on the sodium thiosulphate-iodine system.

one precipitation reaction and one neutralization reaction (shown in Fig. 3) were studied. Each curve gives the result of a single representative titration. The reactions studied were as follows:

Oxidation-Reduction Reactions:

1. $HCrO'_4 + 7H^{\cdot} + 3Fe^{\cdot\cdot} \longrightarrow Cr^{\cdot\cdot\cdot} + 4H_2O + 3Fe^{\cdot\cdot\cdot}$
2. $2MnO'_4 + 2H_2O + 3Mn^{\cdot\cdot} \longrightarrow 5MnO_2 + 4H^{\cdot}$
3. $I_2 + 2S_2O_3'' \longrightarrow S_4O_6'' + 2I'$

Precipitation Reaction:

4. $3Zn^{\cdot\cdot} + 2K_4Fe(CN)_6 \longrightarrow Zn_3K_2[Fe(CN)_6]_2$

Neutralization Reaction:

5. $H^{\cdot} + OH' \longrightarrow H_2O$ $(HC_2H_3O_2 + KOH)$

The accuracy and consistency of the measurements are illustrated by the fact that six consecutive observations made on the system, ferrous ammonium sulfate-potassium dichromate, gave an end-point (taken arbitrarily as the point of inflection of the curve) at 20.30 cc. of the latter solution, with a maximum deviation of 0.05 cc. The end-point determined by the usual potentiometric method also gave 20.30 cc with deviations of the same order. Excellent agreement was found in all cases between the end-points determined by the two potentiometric methods and those determined by the usual volumetric methods, except in the case of the determination of zinc with potassium ferrocyanide where the potential break occurred before (0.2 cc) the volumetric end-point. The results of this titration are in excellent agreement with those of Kolthoff[1] who, using the ordinary potentiometric method, found that the potential break occurred before the equivalence-point was reached.

Conclusion

The simple apparatus which has been described above makes general the application of the electron tube to potentiometric titrations, at least to those reactions which give analytical accuracy when titrated potentiometrically. It has all the advantages of electro-titration, in addition it gives a continuous automatic record of the progress of a reaction, since the electron tube may be regarded as a direct-reading, sensitive voltmeter which draws no current from the titration cell. The apparatus required is inexpensive and readily obtainable, being assembled entirely from standard instruments which are now manufactured in large quantities and at low cost.

Summary

1. An apparatus which makes general the application of the electron tube to potentiometric titrations has been described.

2. Using this apparatus three oxidation-reduction reactions, one precipitation reaction and one neutralization reaction were studied. These

[1] Kolthoff and Furman: "Potentiometric Titrations", p. 268 (1926).

systems were typical of those which give analytical accuracy when titrated potentiometrically.

3. The apparatus described has all the advantages of electro-titration, in addition it has several others which make it suitable for technical and instructional purposes.

Madison, Wisconsin,
December 23, 1926.

ADSORPTION BY METALLIC HYDROXIDES. II. ADSORPTION OF ACIDS, ALKALI AND SALTS BY PRECIPITATED FERRIC HYDROXIDE

BY KSHITISH CHANDRA SEN

Though a certain amount of experimental work exists in the literature on the adsorption of acids and acid ions by colloidal ferric hydroxide in course of its precipitation, no comparative study of the adsorption of acids by precipitated ferric hydroxide seems to have been made. Freundlich[1] cites the experiments of Wöhler, Pluddeman and Wöhler[2] to the effect that ferric oxide adsorbs benzoic acid about ten times as strongly as acetic acid, but besides one or two such references, no systematic attempt has been made. Even the direct estimation of adsorption of ions by colloidal ferric hydroxide has been made by only a few investigators, the reason being that hitherto the order of adsorption of ions has been assumed to be the same as that obtained from the order of the precipitating power of the ions on the colloidal solutions. The usual difficulty of working with precipitated substances however is that the amount of adsorption is generally small and hence the measurements are liable to be in error. As with hydrated ferric, aluminium, and chromium oxides, no such difficulty has been experienced, the adsorption values being quite large, this procedure has been adopted. Two advantages are thereby gained over the colloidal solutions; (1) the amount of the adsorbent may be varied at will in the same volume of the solution and (2) the objection that during coagulation the colloid may adsorb some water does not come in. Further the precipitated substances can be obtained chemically almost pure, and hence the adsorption values will not be vitiated by the presence of other ionic impurities. Owing to these reasons, it was thought advisable to use a freshly precipitated and well washed hydrated ferric oxide as the adsorbent.

The method of experiment was the same as described in the case of arsenious acid. Tht sample of the ferric hydroxide was prepared about twenty-five days before the experiment, and on experimenting showed no ageing effect. The excess of acid in the supernatant liquid was estimated volumetrically by means of carbonate-free alkali using phenolphthalein as the indicator and test experiments showed that the method was quite accurate. To get comparative results, equivalent concentrations of acids were used in almost all cases; only in the cases of formic and acetic acid, a slightly higher concentration was used. The acids were used in rather dilute solutions, so that a high value of adsorption may be obtained and in certain cases dilute solution was necessary to include some of the less soluble acids. The results obtained are shown in Table I.

[1] Freundlich: "Kapillarchemie", 155 (1909).
[2] Z. physik. Chem., **62**, 664 (1908).

TABLE I

Adsorption of acids by hydrated ferric oxide

Amount of oxide = 0.4882 gr.

Vol. = 100 cc; KCl = 0.05 mole per litre

Time = 20 hours

Original strength of the acids = 0.4615 milli-equivalents per 100 cc. The strength of formic and acetic acids was 0.4627 milli-equivalents per 100 cc.

No.	Acid	Amount of adsorption milli-equivalents	Dissociation constant × 10^2
1.	Formic	0.4147	0.021
2.	Acetic	0.3978	0.0018
3.	Monochlor-acetic	0.4326	0.155
4.	Trichlor-acetic	0.4350	———
5.	Propionic	0.3846	0.0013
6.	Butyric	0.3846	0.0015
7.	Valeric	0.3870	0.0016
8.	Caproic	0.3842	0.0014
9.	Benzoic	0.4373	0.0060
10.	m-Oxy-benzoic	0.4349	0.0087
11.	o-Amido-benzoic	0.4325	0.00104
12.	m-Amido-benzoic	0.4253	0.0016
13.	p-Amido-benzoic	0.4300	0.0012
14.	Hippuric	0.4422	0.022
15.	Succinic	0.4422	0.0068
16.	Dibrom-succinic	0.4277	5.0
17.	m-Toluic	0.4349	0.0051
18.	o-Toluic	0.4300	0.012
19.	Malic	0.4470	1.20
20.	Oxalic	0.4470	10.0
21.	Racemic	0.4422	0.097
22.	Meso-tartaric (inactive)	0.4470	———
23.	l-Tartaric	0.4422	0.097
24.	Lactic	0.4277	0.014
25.	Malonic	0.4373	0.158
26.	Citric	0.4470	0.082
27.	Hydrochloric	0.4422 (?)	———
28.	Sulphuric	0.4422	———

Relatively strong acids like hydrobromic, nitric, etc, could not be examined and the result with hydrochloric acid is also somewhat doubtful owing to the ease with which these acids peptise ferric hydroxide. The supernatant liquid was turbid even in presence of .05 mole KCl. It will be evident from these results that at the dilution studied, the amount of adsorption is quite high and the percentage of adsorption lies between 80 to 95 per cent. Obviously in such high adsorptions, the effect of concentration of the original solution

is masked in some cases and, owing to this reason, some of the adsorption values have been found to be equal. A second series of determination was therefore made with varying concentrations of the acids using the same adsorbent, Tables II-XIII.

TABLE II
Adsorption of acetic acid
wt. of Fe_2O_3 = 0.4882 gr.

Conc. of original acid in milli-equivalents	Conc. after adsorption	Adsorption per gram adsorbent
1.3880	0.790	1.225
1.2144	0.640	1.177
1.0410	0.480	1.149
0.8674	0.330	1.102
0.6940	0.200	1.012

TABLE III
Adsorption of propionic acid
wt. of Fe_2O_3 = 0.4882 gr.

Conc. of original acid milli-equivalents	Conc. of solution after adsorption	Adsorption per gram adsorbent
1.9450	1.3110	1.2990
1.5560	0.9600	1.2210
1.1670	0.6100	1.1410
0.9725	0.4303	1.1110
0.7780	0.2800	1.0200

TABLE IV
Adsorption of butyric acid
wt. of Fe_2O_3 = 0.4882 gr.

Conc. of acid milli-equivalents	Conc. of solution after adsorption	Adsorption per gram adsorbent
1.3640	0.7900	1.1760
1.1934	0.6400	1.1330
1.0230	0.4800	1.1120
0.8522	0.3400	1.0690
0.6820	0.2100	0.9668

TABLE V
Adsorption of hippuric acid
wt. of Fe_2O_3 = 0.2559 gr.

1.1320	0.7452	1.5120
0.9057	0.5378	1.4380
0.7924	0.4339	1.4020
0.6792	0.3302	1.3640
0.4528	0.1527	1.1730

TABLE VI
Adsorption of oxalic acid
wt. of Fe_2O_3 = 0.2559 gr.

1.1790	0.5907	2.0650
0.9434	0.4340	1.9910
0.7074	0.2451	1.8070
0.5896	0.1697	1.6410
0.4717	0.0755	1.5480

TABLE VII
Adsorption of sulphuric acid
wt. of Fe_2O_3 = 0.2559 gr.

Conc. of acid milli-equivalent	Conc. of solution after adsorption	adsorption per gram adsorbent
1.1320	0.6981	1.6960
0.9607	0.5381	1.6510
0.8235	0.4150	1.5970
0.6861	0.2922	1.5360
0.5491	0.1699	1.4830

TABLE VIII
Adsorption of citric acid
wt. of Fe_2O_3 = 0.2559 gr.

1.1320	0.4716	2.5810
0.9168	0.2829	2.4770
0.6877	0.1414	2.1350
0.5731	0.0848	1.9080
0.4584	0.0471	1.6070

TABLE IX
Adsorption of malic acid
wt. of Fe_2O_3 = 0.2559 gr.

1.1320	0.6037	2.0650
0.9168	0.4245	1.9250
0.6877	0.2264	1.8030
0.5731	0.1510	1.6500
0.4584	0.0660	1.5330

TABLE X
Adsorption of racemic acid
wt. of Fe_2O_3 = 0.2559 gr.

Conc. of acid milli-equivalents	Conc. of solution after adsorption	adsorption per gram adsorbent
1.1320	0.6414	1.9170
0.8716	0.4056	1.8220
0.6537	0.2358	1.6330
0.5448	0.1425	1.5720
0.4358	0.0660	1.4450

TABLE XI

Adsorption of succinic acid

wt. of Fe_2O_3 = 0.2559 gr.

1.1320	0.7075	1.6590
0.8680	0.4822	1.5120
0.6509	0.2830	1.4370
0.5425	0.1888	1.3820
0.4339	0.1132	1.2530

TABLE XII

Adsorption of benzoic acid

wt. of Fe_2O_3 = 0.2559 gr.

1.1320	0.7735	1.4020
0.9143	0.5700	1.3460
0.7358	0.4057	1.2900
0.5518	0.2641	1.1240
0.3679	0.1038	1.0320

TABLE XIII

Comparative adsorption of some acids when the initial concentration is the same.

Conc. = 1.1320 milli-equivalent per 100 cc

wt. of Fe_2O_3 used = 0.2559 gr.

Acid	Adsorption per gram	Acid	Adsorption per gram
Citric	2.5810	Sulphuric	1.6960
Malic	2.0560	Succinic	1.6590
Oxalic (conc. 1.1790)	2.0650	Hippuric	1.5120
Racemic	1.9170	Benzoic	1.4020

Adsorption of salts and alkali.

In the foregoing pages, the adsorption of acids by hydrated ferric oxide has mainly been given. It has however been shown in the previous paper that both sodium arsenite and caustic soda are adsorbed by ferric hydroxide, and in the case of sodium arsenite mainly the arsenite ion was adsorbed. In this connection the adsorption of many other salts such as potassium sulphate, sodium citrate, sodium phosphate, potassium permanganate, potassium dichromate, etc, by precipitated hydroxide was determined, but, owing to the very small amounts of adsorption, quantitative results could not be obtained. It was however found that with salts like citrate, phosphate, etc, appreciable adsorption of the negative ions takes place on shaking a solution of these salts with ferric hydroxide, a corresponding amount of alkali being set free, which can be tested by means of phenolphthalein. The adsorption therefore seems to be preferential. As it is known that alkali is also adsorbed by ferric hydroxide, a comparative study of the adsorption of acid and alkali seemed desirable. Hence some adsorption experiments have also been made with the ferric hydroxide No. 3 and caustic soda of almost the same concentration as has been used in the case of sulphuric acid. The results are given in Table XIV.

TABLE XIV

Amount of Fe_2O_3 = 0.2559 gr.

Original conc. of NaOH milli-equivalents per 100 cc	Conc. of the soln. after adsorption	Adsorption per grm. adsorbent
0.9434	0.7401	0.7949
0.7548	0.5801	0.6828
0.5659	0.4098	0.6098
0.3773	0.2399	0.5368
0.2830	0.1500	0.5199

It may be assumed that at the dilution studied, both the sulphuric acid and caustic soda are practically completely ionised. Hence if these results are compared to that given in Table VII, it will be noticed that $H^{\cdot}$ ion is much more adsorbed by ferric hydroxide than OH' ions. There is no doubt that this is connected with the chemical nature of the adsorbent, which is a basic substance. A similar instance is known in the case of manganese dioxide.[1] This substance is acidic in nature and it adsorbs both the acidic and basic portions of several substances such as copper sulphate. The adsorption of the basic portion is however much greater than that of the acidic one, and when the adsorption of acids and bases are studied, it is seen that $H^{\cdot}$ ion is much less adsorbed than OH' ions.

Chemical Laboratory,
Allahabad University,
Allahabad,
Feb. 8, 1926.

[1] Dhar, Sen and Ghosh: J. Phys. Chem., **28**, 469 (1924).

THE ADSORPTIVE FORCE OF SILICA FOR WATER

BY P. G. NUTTING*

One of the serious obstacles to the progress of colloid chemistry is the lack of knowledge of the forces involved in adsorption and of the variation of these forces within their minute range of operation. The method here described gives reasonable results checking well with known facts in the case of silica and water. It is rather roundabout; but no more direct method is apparent at present. Heat of wetting is found as a function of thickness; then forces are calculated from its differential.

Parks[1] found the heat of wetting of dry silica by water to be 0.0105 cal/cm^2, independent of the size of the surface and the same for precipitated silica, sand and glass wool. Bellatti and Finazzi[2] determined the heat of wetting of silica having varying moisture content. Their data[3] are reproduced in Table I.

TABLE I

Heat of Wetting of Silica of Varying Moisture Content

A Adsorbed H_2O/gm SiO_2	B Cal/gm of SiO_2	C Cal/gm 26.0−B	D Depth of $H_2O \times 10^6$	E Cal per cm$^2 \times 10^1$
0.00	26.0	0.0	0.0	0.0
0.0238	18.29	7.71	0.95	3.08
.0535	12.33	13.67	2.14	5.47
.0859	9.17	16.83	3.44	6.73
.1292	7.61	18.39	5.17	7.36
.1883	6.50	19.50	7.53	7.80
0.2736	5.25	20.75	10.94	8.30
.3995	3.70	22.30	15.98	8.92
.4635	2.94	23.06	18.54	9.22
.5648	1.66	24.34	22.59	9.74
.6478	0.90	25.10	25.91	10.04
.7694	0.19	25.81	30.78	10.32

Columns A and B are the original data of Bellatti and Finazzi except for the initial value 26.0 obtained by extrapolation. The specific surface of the silica used is 26 ÷ 0.0105 = 25000 cm^2/gm. The water of column A, spread over this surface gives the thickness of adsorbed layer given in D. The heat liberated (in cal/cm^2) by adsorption is given in E.

Parks, in a later paper[4] gives these data and divides E by D thus obtaining cal/cm^2/cm, which is the mean energy density from the silica surface out to

* Published by permission of The Director, Geological Survey.

[1] Parks: Phil. Mag., **4**, 240 (1902).
[2] Bellatti and Finazzi: Atti r. Ist. Venezia, **59**, II (1900); **61**, II, 507
[3] Browne and Mathews in Alexander's "Colloid Chemistry", **1**, p454
[4] Parks: Phil. Mag. **5**, 517 (1903).

the depth shown in D. However the data of real significance is rather to be obtained by plotting E as a function of D and then differentiating this function graphically. This derivative is the rate of decrease of specific energy content with increase of water film thickness outward from the silica surface. The data obtained by this procedure are given in Table II and illustrated by the curves of Fig. 1. Thickness of water film is represented by z in cm $\times 10^6$ and energy by c in cal/cm^2 $\times 10^4$. dc/dz is in cal/cm^2/cm.

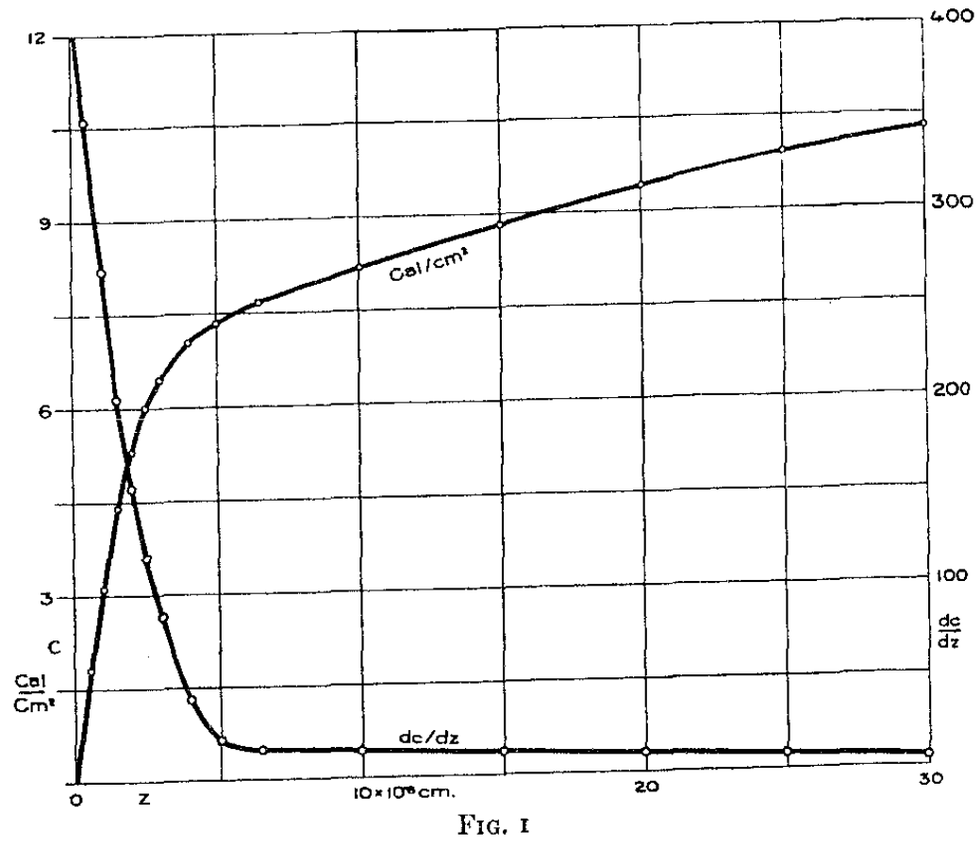


FIG. 1

TABLE II

z	c	dc/dz	P(Atm.)	z	c	dc/dz	P(Atm.)
0.0	0.0	420	17410	5.0	7.32	22.0	912
0.5	1.8	353	14630	7.5	7.72	16.5	684
1.0	3.1	274	11360	10.0	8.18	15.1	626
1.5	4.4	205	8500	15.0	8.82	12.1	502
2.0	5.3	157	6510	20.0	9.42	11.5	477
2.5	6.0	120	4970	25.0	9.94	8.7	361
3.0	6.45	88	3650	30.0	10.28	5.6	232
4.0	7.04	44.5	1845				

The differential curve turns sharply at thicknesses between 4 and 5 $\times 10^{-6}$ cm representing a layer of water between 100 and 120 molecular diameters deep. It is straight and steep near the origin indicating a high but uniformly decreasing rate of falling off in the energy of adsorption. That energy is by no means confined to the first molecular layer nor is there any apparent break after the first. Dissociation of water into H and OH is indicated but not

proven by this curve without additional data on the rate of decrease in density. Since the depths of water were determined by weighing, increased densities due to close packing of staggered H and OH ions or by actual compression would have the effect of slightly compressing the abscissae near the origin and therefore of enhancing the slope of the energy curve. On the other hand, dissociation would use up energy (at the expense of adsorptive forces) and therefore flatten both curves. Further out, beyond a layer about 175 molecules deep, the differential curve becomes very low and again of uniform slope.

Interest centers on the two straight portions of the differential curve. Near the silica surface ($z = 0$) the slope is uniformly 143×10^6 cal/cm^2/cm^2, and for that straight portion (in cal/cm^2/cm)

$$dc/dz = 420 - 143\ z$$

Reducing calories to ergs by means of the factor 42×10^6 ergs/calorie (J) and remembering that $Jdc = Pdz$ where P is the pressure in dynes/cm^2 we get

$$P = (17640 - 6006\ z) \times 10^6 \text{ dynes/cm}^2$$
$$= 17410 - 5928\ z \text{ in atmospheres.}$$

In these equations z is still in the units of the table and figure, namely 10^{-6}cm.

The maximum pressure (at the surface, $z = 0$) of 17410 atmospheres, is moderate compared with some estimates running as high as 37000 atm. arrived at by differential density determinations, known compressibility and estimates of thickness. This simple law of force (P above) is reasonable and holds very well for a thickness of at least 50 molecular diameters, fairly well to 100 where evidently conditions are modified. If conditions existing near the surface held indefinitely, the pressure would fall to zero ($P = 0$) at $z = 2.94 \times 10^{-6}$ cm or 73 molecular diameters. The pressure gradient near the surface, namely 5928 atm/10^{-6} cm = 237 atmospheres per molecular layer of water 4×10^{-8} cm deep. Allowing for the known compressibility of water in compressing the z scale near the origin (region of high pressures) this maximum pressure gradient (237 atm./molec. diam.) would be reduced and the pressure gradient curve straightened still further, out to about $z = 4 \times 10^{-6}$ cm. There is no apparent justification for attempting to fit an inverse power law to the falling off of force with distance. It can be done with a double exponential but the fit is not as good and the formula has no rational physical basis.

The slope of the differential (dc/dz) curve falls to 0.450 cal/cm^2/cm^2 at a distance from the silica surface (lower straight portion). For this portion of the curve

$$dc/dz = 19.6 - 0.450\ z \text{ (cal/cm}^2\text{/cm)}$$

and reducing to pressure as before

$$P = (824 - 18.9\ z) \times 10^6 \text{ (dynes/cm}^2\text{)}$$
$$= 813 - 18.6\ z \text{ (atmospheres)}$$

from which $P = 1$ for $z = 43.7 \times 10^6$ cm $= 0.41\mu = 1090$ molecular diameters of water (4×10^{-8} cm = 4 A.U.) If this same pressure gradient existed back to the surface $z = 0$, the pressure then would be $P = 813$ atm. Within this region of uniform pressure gradient, the pressure falls off at the rate of 0.74 atm. per molecular layer of water.

The pressures and pressure gradients deduced above for the adsorption of water on silica are reasonable from many angles and point the way to further deductions in the realm of hydration and solution. It is not to be overlooked that if the solid pulls on the adsorbed liquid, the liquid must pull on the solid. The pull deduced above (17000 atm.) for the maximum exerted by silica on water is of the same order as the tensile strength of quartz. Hence if the water molecules (or H and OH ions) can but secure a proper toe hold or arch themselves, they would be expected to pull the silica out into solution, or into hydration at least. Even quartz does in fact slowly hydrate and go into solution and suspension. I have obtained over half a gram per liter in permanent suspension from powdered silica heated for six hours in distilled water in a platinum dish.

Liquid solvents for solids must therefore be adsorbed by the solid with a maximum force exceeding its tensile strength and solution will continue until equilibrium is restored by the added pressure of material in solution. The adsorption of water on silica involves considerable release of energy partly because of the low stability of silica in water. If soda (or potash) be added to the water, the sodium ions are still more strongly adsorbed than the water but they pull the silica into solution, thus using up (in dissociating and expanding the silica) the energy released by adsorption.

U. S. Geological Survey
Washington, Oct. 1926.

THE VELOCITY OF REACTION AND ENERGY OF ACTIVATION OF HALOGEN COMPOUNDS

BY DAVID HENRY PEACOCK

In a very large number of cases certain regularities have been observed in the effect of substituents upon the reaction velocity of halogen compounds with other reactants such as water, amines, sodium allyl oxides, and potassium iodide. The alternating character of these effects has been extensively studied in connection with the theories of Flurscheim and of Lapworth and Robinson. It has been shown by the present author[1] that this alternating character is also observed in the energy of activation of *m*- and *p*-nitrobenzyl chlorides with aniline, *p*-toluidine, *o*-toluidine and dimethylaniline. A tertiary base was used because with a primary or secondary base there is always the possibility of two reactions (1) the formation of a salt of pentavalent nitrogen (2) direct removal of hydrogen from combination with the nitrogen. The latter possibility may be considered as somewhat remote in the reactions under consideration.

It has now been found that methyl-ethyl-aniline with *m*- and *p*-nitrobenzyl chloride and dimethyl-*m*- and *p*-toluidine with benzyl chloride also show this alternating effect. The measurements were carried out in a manner similar to those already described (loc. cit.) and are given in Table I.

TABLE I

Energies of Activation:—Tertiary Bases

Methyl alcohol solution at 35°C and 45°C.

[Base] = 0.4M, [Halogen compound] = 0.1M

	k_{35}	E
Ethyl methyl aniline and meta-nitrobenzyl chloride.	5.01×10^{-4}	8335
" " " " para- " "	3.01×10^{-4}	8964
Dimethyl-para-toluidine and benzyl chloride	6.58×10^{-3}	13470
" meta- " " " "	4.74×10^{-3}	14850

The second case is interesting as showing the alternating effect of a methyl group upon the energy of activation of the nitrogen atom in the reaction concerned. Similar cases are being studied. The work of Holleman[2] on the rates of hydrolysis of substituted benzyl chlorides provides data from which a series of energies of activation can be calculated, Table II.

It is apparent that with exception of the first pair of reactions that reaction which is faster has the smaller energy of activation. Holleman (loc. cit.) drew attention to this in another way by stating that the differences between the reaction velocities tended to become smaller as the temperature increased.

[1] Peacock: J. Chem. Soc., **127**, 2177 (1925).

[2] Rec. Trav. chim., **41**, 646 (1927).

TABLE II

Energies of Activation: Hydrolysis Reaction
(Holleman: loc. cit)

Halogen compound	k (30°)	$k_{3}/k_{35}°$	E/10^4
p-$CH_3.C_6H_4.CH_2Cl$	1.04	157	2.04 cals.
m- ,,	0.144	150	2.01
p-$Cl.C_6H_4.CH_2Cl$	0.052	184	2.10
m- ,,	0.0152	242	2.21
p-$BrC_6H_4CH_2Cl$	0.0457	170	2.07
m- ,,	0.0147	227	2.18
p-$NO_2.C_6H_4CH_2Cl$	0.00491	234	2.19
m- ,,	0.0063	222	2.17

From the results given by Holleman[1] it is possible to calculate the energies of activation for the reaction between nitro 2:4 dichlorobenzene or nitro 2:5 dichlorobenzene and sodium methoxide in one case and diethylamine in the other. The results are collected below:—

(1) Sodium Methoxide.

	Nitro 2:4 dichlorobenzene	Nitro 2:5 dichlorobenzene
	$k_{25} = 0.030$	0.0063
	$k_{50}/k_{25} = 2.09$	1.92
	E (50/25) $= 2.31 \times 10^4$	2.24×10^4
	$R_{85}/R_{50} = 3.09$	3.24
	E (85/50) $= 2.24 \times 10^4$	2.27×10^4

(2) Diethylamine

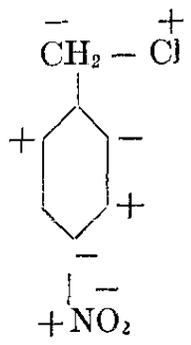
$k_{85}°$	0.027	0.0067
R_{110}/R_{85}	3.15	3.43
E (110/85)	1.36×10^4	1.34×10^4

The faster reaction has the smaller energy of activation in only one pair of these results namely in the reaction between sodium methoxide and nitro 2:5 dichloro benzene at 50°C and 85°C. It must be remarked however that in nitro 2:4 dichloro benzene both chlorine atoms are labile (cf Holleman: loc. cit. for velocity coefficient with *o*- and *p*-nitrochloro benzene) and this is bound to complicate the results.

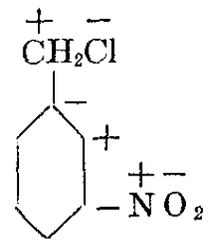
If the hypothesis of Robinson and Lapworth with regard to the alternating effect of substituents upon the reactivity of a labile atom be interpreted in the sense that of two compounds that is more reactive which is activated more easily and if this interpretation be applied to the cases tabulated above it will be seen that where the hypothesis demands that one substance should be more reactive than another then the energy of activation of the more reactive substance is less than that of the less reactive, e.g.:

[1] Rec. Trav. chim., 35, 1 (1915).

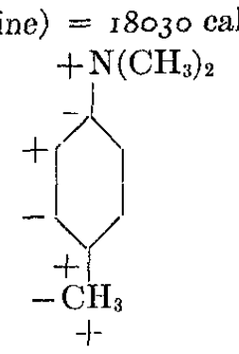
Methyl benzyl chloride ($CH_3.C_6H_4.CH_2Cl$) does not behave in accordance with the hypothesis and the results given by nitro 2:4 dichloro and 2:5 dichloro benzene are contradictory. Bearing in mind the difficulty of obtaining accurate results for the energy of activation the agreement between the order of these values and those predicted by the Robinson and Lapworth hypothesis seems too close to be fortuitous and supports the assumption that the energy of activation of a substance shows alternating effects which can be predicted with the help of the Lapworth-Robinson hypothesis. It is of course understood that the term energy of activation of a substance means energy of activation with a particular reactant.



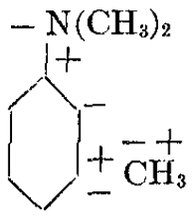
E (aniline) = 18030 cals.



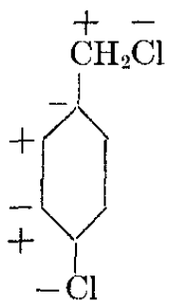
E (aniline) = 17280 cals.



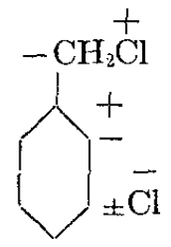
E (Benzyl chloride) = 13410 cals.



E (Benzyl chloride) = 14850



E (water) = 2.10×10^4 cals.



E (water) = 2.21×10^4 cals.

In passing it may be remarked that the relative reactivities of the *m*- and *p*-dimethyl toluidines while in accordance with the Lapworth and Robinson hypothesis do not agree with the Flurscheim hypothesis as ordinarily applied. Toluene shows reactivity in the *o* and *p* positions and therefore according to the Flurscheim hypothesis the nitrogen atom in the *m* position should possess excess of residual affinity and be more reactive than the nitrogen atom in the *p* position, the opposite is actually the case. Further work is proceeding on this subject.

The temperature coefficients of two simultaneous reactions will naturally affect the relative amounts of the products formed. If the faster reaction has the greater temperature coefficient then the proportion of product formed in the greater amount will increase as the temperature rises. If, on the other hand, the product formed in the greater amount is produced by a reaction with a lower temperature coefficient i. e. a smaller energy of activation, then the relative amounts of the two products will approach one another as the temperature rises and may even change in ratio. Conclusions as to reactivity based on the relative quantities of two products formed at a particular temperature would thus appear to attach undue importance to relative velocities at an arbitrary temperature.

In the cases considered the alterations in velocity were produced by the alternating effect of a particular substituent and the difference in velocities is much more marked than the difference in energies of activation. If instead of examining the effect upon velocity of the change in position of a particular substituent we study the effect of substituting one halogen for another then the difference in velocities is often of a much higher order than the difference of temperature coefficients and therefore of energies of activation. Perhaps the earliest case studied is the reaction velocities of allyl halogen compounds with sodium and potassium ethoxide oxamined by Conrad and Bruckner[1] who found that the relative rates of reaction for chlorides, bromides and iodides were approximately as 1:70:140 while the temperature coefficients of all three reactions were approximately the same. Menschutkin[2] found that the relative rates of reaction for alkyl chlorides, bromides and iodides with amines were approximately as 1:100:700. The temperature coefficients and energy of activation for one particular amine with the halogen derivative of a particular allyl compound in the same solvent do not seem yet to have measured but from the results of Jones and Preston[3] the energy of activation for the reaction between allyl iodide and dimethylaniline is found to be 9362 and for tri isoamyl amine 9702 in absolute alcohol. The velocity constant for the first reaction at 25°C was 0.656. E. R. Thomas[4] for the velocity constant of the reaction allyl bromide and dimethyl aniline found the value 1.08 at 40°C in absolute alcohol. The iodide would thus react probably twice as fast at the same temperature. Measurements have been made of the velocity constants of the reaction between diethyl aniline and benzyl chloride and benzyl bromide in methyl alcohol; the constants at 35°C are .000178 and .00473. The energies of activation for the same reactions[5] are 14550 and 15560. These results are tentative. Slator and Twiss[6] examined the rates of reaction of a number of halogen compounds with sodium thiosulphate. Some of their results are given in Table III.

[1] Z. physik. Chem., **4**, 531 (1889).
[2] Z. physik. Chem., **5**, 589 (1890).
[3] J. Chem. Soc., **101**, 1930 (1912).
[4] J. Chem. Soc., **103**, 592 (1913).
[5] $C_6H_5N(C_2H_5)_2$ = 0.8 M in benzyl chloride reaction and 0.4 M in benzyl bromide reaction.
[6] J. Chem. Soc., **95**, 99 (1909).

TABLE III

Rates of Reaction and Temperature Coefficients for Alkyl Halides and Sodium Thiosulphate

CH_3I	$k_{15}° = 0.280$	$(k_t + 10°)/k_t = 3.05$	Iodides
$CH_2ICOOC_2H_5$	$k_{15}° = 2.55$	" = 2.75	Iodides
CH_3Br	$k_{15}° = 0.29$	" 3.1	Bromides
$CH_2BrCOOC_2H_5$	$k_{15}° = 2.36$	" 2.75	Bromides
CH_3Cl	$k_{15}° = 0.0066$	" 3.2	Chlorides
$CH_2Cl.COOC_2H_5$	$k_{25}° = 0.060$	" 2.9	Chlorides

The final impression produced by all these results is that while the substitution of one halogen for another may make a large effect on the velocity constant the effect on the energy of activation is very small. If the energy of activation is related to the stability of the halogen linkage in the allyl compounds then it is probably also related to the energy required to displace the electrons constituting that bond and to the energy required to break the bond. No data seem available bearing directly on this point but it is significant that the heats of combustion of halogen compounds show no large differences and are usually of the order RCl > RBr > RI. Indirect evidence as to the stability of the HX electronic bond is perhaps afforded by the following figures as to their ionisation potentials given by Mackay[1] HCl = 13.7 HBr = 13.3 HI = 12.7 volts. The hydrogen compounds are not the most suitable to choose in view of the peculiarities of hydrogen but no other data seems available.

Two other points are of interest in this connection. Menschutkin[2] found that in benzene solution the reaction velocity of *m* toluidine with allyl bromide was greater than that of *p*-toluidine and so also with methyl bromide. In acetone solution however both bromides reacted faster with *p*-toluidine. In the case of allyl bromide it was found that also in brom naphthalin *m*-toluidine reacted faster than *p* whereas in acetophenone and propyl alcohol the *p*-compound reacted faster. The effect of a methyl group in the *m* or *p* position thus depended on the solvent. With 2:4 dimethyl aniline and 2:5 dimethyl aniline the compound with the methyl group in the *p* position reacted faster than the *m* in both benzol and acetone. Thus the anomalous effect of a methyl group in the *m* or *p* positions is shown only by *m*- and *p*-toluidine in certain solvents.

Rheinlander[3] found that the substitution of iodine for chlorine in 2:4 dinitro chloro benzene produced anomalous results in that the reaction velocity of dinitro-iodo-benzene with certain bases was lower than that of dinitro-chlorbenzene. The effect then of a change in the position of a substituent upon reaction velocity may depend upon the solvent used and the effect of substituting iodine for chlorine depends on the reaction studied.

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[1] Phys. Rev., (2) **24**, 324 (1924).
[2] Z. physik. Chem., **34**, 157 (1900).
[3] J. Chem. Soc., **123**, 3099 (1923).

Such considerations raise the question as to the suitability of velocities of reactions as a measure of reactivity. One obvious disadvantage which has been referred to by Haywood[1] is that the order of velocities may depend on the temperature chosen for their measurements if their temperature coefficients are unequal. Haywood endeavoured to get over this difficulty by measuring the ratio of the velocities under condition of equal entropy change i. e., where Q/T was constant and found that under these conditions the velocity ratios were constant. This result however follows at once from the fact that Q is calculated from the ordinary equation $d \log k/dt = Q/RT^2$. Haywood's results have been criticised on other grounds.[2]

If by the reactivity is meant the ease with which a compound may be brought to the reactive state or activated condition then it is difficult to resist the conclusion that energies of activation or some quantity closely connected with them are the true measure of this property. The theories which have been brought forward to explanation in varying reactivity suffer no distortion if the above meaning is attached to the term but may perhaps be considered to acquire a greater degree of precision. Energies of activations are less susceptible of accurate comparison than velocities of reaction but the latter quantities seem made up of two factors, only one of which can be easily seen to depend on structure.

Several equations have been suggested for expressing the velocity of a bimolecular reaction in terms of other molecular constants. Dushman[3] suggests the equation:

$$k = N\sigma^2\sqrt{8\pi RT\,(1/M_A + 1/M_B)}\,\sqrt{e^{-}\,(Q_A + Q_B)\,/\,RT}$$
$$\text{or } k = e^{-Q/RT}$$

If we restrict ourselves to reactions such as those between aniline and *m* or *p* nitrobenzyl chloride then M_A and M_B will be the same in the two cases and the values of σ will probably also be very close. The same remarks apply to all reactions in which *m* and *p* isomers are compared with a fixed reactant. If then the velocities for such a pair of reactants be compared at equal temperatures we have:

$$\log_e k_p = \log_e A_p - Q_p/RT$$
$$\text{and } \log_e k_m = \log_e A_m - Q_m/RT$$

If $A_m = A_p$ as assumed above, then $\log_e k_p - \log_e k_m = 1/RT\,(Q_m - Q_p)$ or $RT \log_e k_p/k_m = Q_m - Q_p$.

where Q_m = sum of the energies of activation for the fixed reactant A, and the *m* isomer i. e. $Q_m = Q'_A + Q'_m$ and so with Q_p.

In Table V are collected values for $RT \log_e k_p/k_m$ and of $Q_m - Q_p$ for several reactions; the hydrolysis of substituted benzyl chlorides was studied by Holleman (loc. cit.) the other results are by the present author.

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[1] J. Chem. Soc., **121**, 1904 (1922).
[2] Cf. Goldsworthy: J. Chem. Soc., **1926**, 1102.
[3] J. Am. Chem. Soc., **43**, 397 (1921).

TABLE IV

Velocity Constants and Energies of Activation for *m* and *p* Substituents.

(a) Hydrolysis Reaction T = 303°

Reactants.	log (k_p/k_m)	RTln (k_p/k_m)	$Q_m - Q_p$
m and *p*- $CH_3.C_6H_4.CH_2Cl$	0.8586	1506	−300
m- and *p*- $Cl.C_6H_4.CH_2Cl$	0.5342	745	1100
m- and *p*- $Br.C_6H_4.CH_2Cl$	0.4926	688	1100
m- and *p*- $NO_2\ C_6H_4.CH_2Cl$	−0.1082	−149	−200
(b) *m*- and *p*-nitrobenzyl chloride T = 308°			
Aniline	−0.1088	−154	−750
p-Toluidine	−0.1687	−239	−2620
o-Toluidine	−0.1698	−240	−3470
Dimethyl aniline	−0.2203	−310	−2840
Ethyl methyl aniline	−0.2212	−312	−629
(c) Benzyl chloride T = 308°			
m- and *p*-dimethyl toluidine	0.1424	201	1380

The lack of agreement between the values of RTln k_p/k_m and $Q_m - Q_p$ may indicate either experimental error in the determinations or lack of equality between A_m and A_p. Certain interesting relationships appear however when the results are examined and it is proposed to study these more fully. The ratio k_m/k_p for *o*-toluidine is practically equal to that for *p*-toluidine while that for dimethyl aniline is practically equal to that for ethyl methyl aniline. This indicates that for each reaction $A_m = A_p$ and also that $Q_m = Q'_A + Q'_m$. Therefore, $Q_m - Q_p = Q'_m - Q'_p$, constant as long as the *m* and *p* isomers react with substancies of similar constitution.

A *strict comparison* between chlorine, bromine, and iodine compounds cannot be made because all the necessary data are not known but the results of Conrad and Bruckner (loc. cit.) show that with alkyl oxides the temperature coefficients of the reaction velocities are approximately equal while the actual velocities vary very greatly; thus there is a greater discrepancy between the values of E_1/E_2 and $\frac{\log k_1}{\log k_2}$ than would be expected from the variation in σ and molecular weight in passing from one halogen compound to another. A reference to the discussion of the reaction velocities of chlorine, bromine and iodine compounds with amines and with sodium thiosulphate shows that here also the velocity constant show much greater variation in value than is shown by the energies of activation. Energies of activation like heats of combustion and ionisation potentials show only small changes in passing from chloro to bromo and iodo compounds.

It therefore follows that the equation for a bimolecular reaction is of the type: $k = k_1\ e^{-Q/RT}$ where k_1 is a constant much more dependent on the

constitution of the compounds concerned than the expression involving molecular diameters and molecular weights. Perrin and Job suggest that this term represents the sensibility or ease of activation of the molecules.

It is also possible that k_1 represents some function of the stability of the activated molecule. The high rates of reaction frequently observed with iodo compounds may then be due mainly to the longer life of the activated molecules of the iodo compound as compared with those of a bromo or chloro compound. Similarly the very much greater reactivity of *o*- or *p*-nitro bromo benzene as compared with m nitro brom benzene may be ascribed not entirely to an alternating effect on the energy of activation but also to an effect on the stability of the activated state. It is also possible that the effect of the solvent on reaction velocity may be partly due to the same cause.

A comparison of reaction velocities or what is the same thing of the quantities of isomers formed in a particular reaction thus involves two quantities at least, the energy of activation and another quantity which may be the sensibility to activation, the stability of the activated molecule or a combination of both.

Summary

(1) Attention is drawn to the alternating effect of substituents upon the energy of activation for the reactions studied.

(2) The effect of energy of activation in altering the ratios of velocities and therefore the ratios of the products formed, at different temperatures is pointed out.

(3) It is suggested that the alteration in activation energy is a more truthful expression of the effect of substituents upon reactivity than is the velocity of the reaction.

(4) A comparison is made of the effect of substituting one halogen for another upon the velocity constant and energy of activation for a number of reactions. The order of energies of activation is compared with the order of ionisation potentials for the halogen acids.

(5) Velocities of reaction are affected not only by alterations in activation energy but also by variations in the sensibility of the molecule (Perrin, Job) and the stability of the activated state.

(6) The applicability of Dushman's equation to the cases concerned is examined.

University College
University of Rangoon
Sept. 20, 1926.

THE EFFECT OF HIGHER ALIPHATIC ACIDS ON THE SURFACE TENSION OF A HEAVY HYDROCARBON OIL*

BY E. C. GILBERT

The surface tensions of solutions of fatty acids in aliphatic and aromatic hydrocarbons both at liquid-vapor and liquid-liquid interfaces have been reported by various investigators[1] but little is known concerning the longer chain acids and the heavier hydrocarbons. The present study was initiated because of its bearing on the effect of small quantities of fatty acids on the properties of lubricating oils.

Materials

For the hydrocarbon "Liquid Petrolatum Squibb" was chosen. It is described as a pure naphthene from California crude. It had no odor, and practically no water content (as shown by placing freshly cut sodium in it). It contained no paraffin or sulfur compounds and possessed a density at 20°C, of 0.8845. It was of course chemically a mixture. "Nujol," described as a pure paraffin oil, would have been preferable to a naphthene from a theoretical standpoint but the Nujol available showed a higher water content. The surface tensions and solubility relationships were very similar as shown by preliminary investigation not reported, so the Squibb's oil was used thruout.

The fatty acids used were myristic, $C_{14}H_{28}O_2$, M.P. 52°-53°, and pelargonic, $C_9H_{18}O_2$, M.P. 10°-12°, the latter being a liquid at ordinary temperatures. Both were obtained from the Eastman Kodak Co. The myristic acid was quite soluble in the hydrocarbon at higher temperatures but not very soluble at 20° (considerably less than 0.4 mols per 1000 g.). The pelargonic acid was miscible in much higher proportions.

Procedure

A series of dilute solutions of each acid was made up by weight, using a stock solution containing 0.371 mols per 1000g. as a source of myristic acid, and by direct addition of the liquid pelargonic acid. These solutions were made and preserved in flat glass stoppered bottles of 5-6 cm. diameter. After the acid was added the solutions were heated to 120°C. in an oven and well stirred to secure even mixing. They were then allowed to cool down overnight in a large room of very constant temperature. Care was taken to have all apparatus scrupulously clean. Densities of the solutions of highest and lowest concentration were determined by the use of a picnometer, and for intermediate concentrations were interpolated.

The surface tensions were determined by the use of the du Noüy tensiometer[2] which had been calibrated against water, benzene, and bromobenzene by the recently published method of Harkins, Young, and Cheng.[3] The

* Contribution from the Department of Chemistry, Oregon State College.

[1] King: Kansas Expt. Sta. Tech. Bull., 9, (1922); Harkins and others: J. Am. Chem. Soc., 39, 354, 541 (1917); **41**, 970 (1919); **42**, 700 (1920); **43**, 51 (1921); **44**, 2665 (1922).

[2] du Nouy: J. Gen. Physiol. **1**, No. 5 (1919).

[3] Harkins, Young, and Cheng: Science, (2), **64**, 333 (1926).

ratio, radius of ring to radius of wire in the ring, was 32.02. The radii were measured carefully with a travelling microscope. The apparatus was tested to see that the torsion was proportional to the pull on the ring. The graph was a straight line. A long, rigid, pointed wire was affixed to the beam, opposite to which was another sharply pointed wire adjusted so that at the zero reading of the instrument the two points coincided. This aided materially in maintaining the beam in zero position as the movement of the beam was

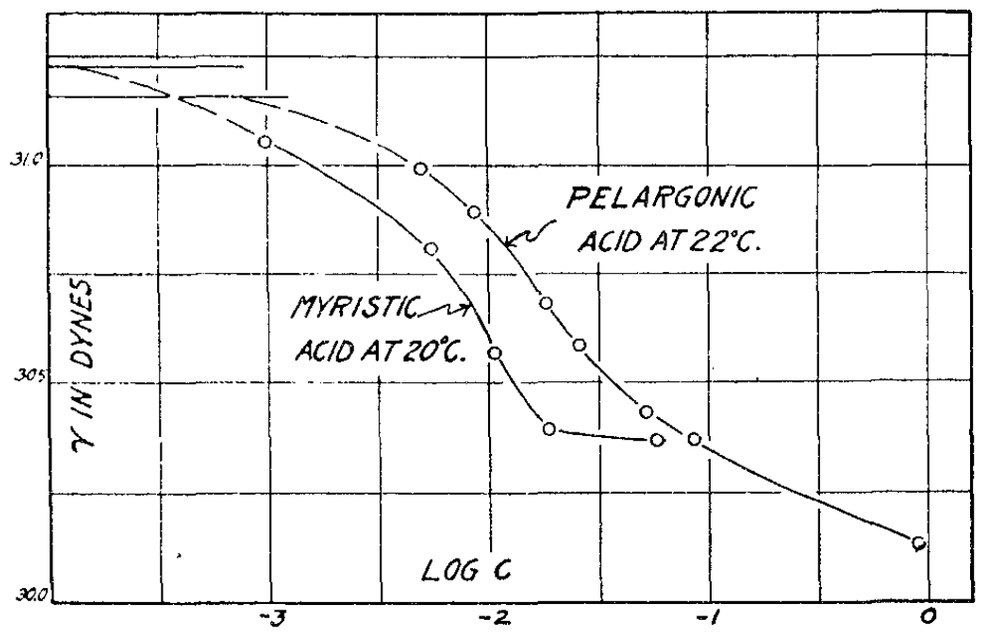


FIG. 1

magnified. The instrument was always adjusted for the zero point with the ring wet. The readings were readily duplicated and the absolute values are believed to be accurate to ±1%, the relative readings being more accurate than that. For the pure Squibb's oil at 20° a value of 31.23 dynes per cm. was obtained. A value of 31.12 was reported for a sample of similar Squibb's oil in 1922, using the very accurate drop-weight method.[1] A large vacant room was used and the constancy of temperature was such that a constant temperature bath was not required.

Without the precautions and corrections made as directed by Harkins and his collaborators the ring method gives results much too high. For the Squibb's oil the apparent surface tension by this method was 34.60 dynes. The corrections are somewhat lengthy of explanation and the reader is referred to the original article.

Results

The results are tabulated in Table I. The surface tensions were plotted against logarithm of the concentration in Fig. 1, and the adsorption of the acid on the surface of the hydrocarbon calculated from the equation of Gibbs, $U = -1/RT \cdot \delta\gamma/\delta \ln C$. When $\delta\gamma/\delta \ln C$ becomes constant it is com-

[1] Harkins and Feldman: J. Am. Chem. Soc., **44**, 2665 (1922).

monly assumed that the surface has become covered with a layer of the solute one molecule thick[1] and on this basis the area covered by each molecule was calculated.

TABLE I

Surface Tension of Solutions of Myristic Acid at 20°C. and Pelargonic Acid at 22° C. in Liquid Petrolatum (Squibb)

Conc. Mols per 1000 g. of oil		Density	$\frac{Mg}{4\pi R}$	γ dynes per cm.^{2}	$\frac{\delta\gamma}{\delta \log C}$	U × 10^{10} Mols per cm.^{2}
0.0000		0.8845	34.60	31.23		
0.00098	(Myr.)	0.8845	34.42	31.05	0.177	0.032
0.00561	"	0.8846	34.18	30.81	0.571	0.102
0.0107	"	0.8847	33.93	30.57	0.865	0.154
0.0197	"	0.8850	33.75	30.39		
0.061	"	0.8859	33.75	30.37		
0.00832	"	interpolated on graph			0.800	0.143
0.0000		0.8838	34.54	31.16		
0.0087	(Pel.)	0.8838	34.24	30.89	0.473	0.077
0.01826	"	0.8838	34.06	30.68	0.70	0.124
0.02593	"	0.8839	33.95	30.58	0.70	0.124
0.0517	"	0.8839	33.81	30.43		
0.0845	"	0.8840	33.75	30.37		
0.9248	"	0.8865	33.51	30.13		
0.0138	"	interpolated			0.74	0.131

Discussion

The curves for the two acids, surface tension-log C are very similar to each other. The pelargonic acid, being more soluble, gives correspondingly less lowering of the surface tension for the same concentration. Both curves follow the general form observed when the solute lowers the surface tension of the solvent and is positively adsorbed in the surface, but both are characterized by a sudden change in the slope of the curve when only a relatively small lowering of the surface tension has occurred. Beyond a concentration of 0.06-0.08 M there is only a lowering of less than 0.3 dyne for a 10-fold change in the concentration in the case of pelargonic acid, and the flattening of the curve for myristic acid begins even at a concentration of 0.02 M. This sudden change of slope occurs just after the surface has been covered by the monomolecular layer. The sudden flattening of the curve therefore seems to indicate that beyond this point of saturation of the surface layer the surface tension observed is predominantly that of the material in the surface rather than that of the solvent. The actual total lowering is rather small, only one dyne at the most, for the concentrations observed. This in marked contrast to the behavior of water but is due to the fact that the surface tension of the acids is not far below that of the oil.

[1] Langmuir: J. Am. Chem. Soc., 39, 1848 (1917).

The question of the orientation of the molecules in the surface layer is interesting in this case since we have a situation just reversed from that of the fatty acids in water. Here in this experiment we should expect the long hydrocarbon chains of the acids to be soluble in the body of the solvent and the polar carboxyl groups forced to the surface. In the case of myristic acid the slope $\delta\gamma/\delta$ logC becomes constant at C = 0.0083 M and remains so approximately to C = 0.02 M. In this range U = 0.15×10^{-10}. Assuming a density at 20° of 0.88 (d = 0.858 at 60° C.) this gives a thickness of only 0.4×10^{-8} cm. for the surface layer and an area of 11×10^{-14} cm.^{2} per molecule. These are sufficiently far from the data of Langmuir to indicate that here the similarity between solute and solvent is so great that each solute molecule may have associated with it a number of solvent molecules. This is supposed to be the case with acetic acid and water where the dimensions of molecules calculated from surface tensions are at variance with those expected.[1]

With pelargonic acid the surface layer is saturated only at a higher concentration (C = 0.014 M) due to greater solubility; U = 0.13×10^{-10}, and the calculated thickness only 0.22×10^{-8} cm.

If the molecules are assumed to lie on their side in the surface the observed dimensions are not so far from the expected, as then the calculated thickness would be of the order of 4×10^{-8} cm. It is more than likely that such is the case, but there still are not enough acid molecules to cover the surface, completely excluding all solvent molecules.

Summary

The surface tensions of solutions of pelargonic and myristic acid in a pure heavy hydrocarbon oil have been determined by the ring method, as modified by Harkins.

From these the adsorption of the acids on the surface of the oil has been calculated, also the apparent thickness of the surface layer and the area per molecule.

The surface tension dropped quite rapidly at small concentrations until shortly after the surface layer became saturated, beyond which point increased concentration had an extremely small effect.

The calculated thickness is too small and the area too great indicating that probably the molecules of solute and solvent are sufficiently similar so that solvent molecules are not completely excluded from the surface.

Corvallis, Oregon.

[1] Langmuir: loc. cit.

THE ELECTRICAL CONDUCTIVITIES OF SOME SOLUTIONS IN ANILINE

BY JAMES ROBERT POUND

Frequently the electrical conductivities of non-aqueous solutions are of a different order of magnitude to those of aqueous solutions. Also often the former vary with the concentrations of the solutions in a different manner to the well-known behaviour of aqueous solutions; in the latter solutions the equivalent conductivity, A, rises as the concentration decreases and reaches a more or less definite maximum, A_o, but in many non-aqueous solutions the equivalent conductivity falls as the concentration decreases and approaches the value zero at zero concentration.[1] The present paper deals chiefly with the electrical conductivities of some solutions in aniline at 30°.

Qualitative Experiments. Two platinum wires were connected through an electric lamp to the city 220 volt D.C. supply. The wires were placed about half a centimetre apart in various solutions in aniline; and when the current was turned on, the effects were noted. With a few of the best conducting solutions the lamp lit up. In the conducting solutions there was evolution of gas (hydrogen?) at the cathode with more or less rapidity, and at the anode a dark brown solution appeared and slowly mixed with the bulk of the liquid, which was usually of a light brown colour. These two effects were taken as indications of the conducting power of the solution. If a solution was a poor conductor and gave no gaseous products on electrolysis, then these experiments would fail to indicate its conducting power. The solutions were of indefinite strength; but if the solute was not very soluble they were saturated. The experiments were done cold and then hot—up to the boiling point of aniline. The aniline was distilled pure aniline (v. later), and the solutes were the best commercial products, taken as dry, which certainly was the case with most of them. The presence of water usually increased the conducting power. The solubilities of the solutes varied greatly. More than one hundred substances were tested in this manner.

Conducting solutions with aniline were given by the acids and their anhydrides and by the salts of organic bases (if these substances were at all soluble). Such were acetic acid, acetic anhydride, phthalic acid, phthalic anhydride, salicylic acid, phenylacetic acid, succinic, picric, hippuric, sulphosalicylic, sulphoanilic and other sulphonic acids, monochloracetic acid, rosolic and pararosolic acids; aniline hydrochloride, m-phenylenediamine hydrochloride, 'methyl violet' or pentamethylpararosaniline hydrochloride, and similar salts, and saccharin. The conductivities of the first six substances and of aniline hydrochloride and saccharin were investigated quantitatively (v. later), as also were the conductivities of benzoic acid in aniline. Benzoic

[1] C. A. Kraus: "The Properties of Electrically Conducting Systems" (1922); Pound: J. Chem. Soc., **99** (1911); **121** (1922); **125** (1924).

acid, though freely soluble in aniline, gives very poorly conducting solutions, which in these qualitative experiments were classed as non-conducting; thus some of the following non-conducting solutions may be similar to those of benzoic acid. The stronger an acid, the better conducting is its solution in aniline, unless it forms anilides which give poorly conducting solutions (v. later). The salts (hydrochlorides) of complex bases, like methyl violet, seem to give poorer conducting solutions than the salts of simpler bases; but this may be largely due to their differing solubilities.

The substances that gave non-conducting solutions with aniline were (1) most salts, e.g. potassium cyanate, sodium oxalate, quinine sulphate, aniline sulphate, calomel and zinc valerianate. Most of these salts were very sparingly soluble. (Mercuric chloride is not very soluble in cold aniline; but, on warming, the mixture suddenly turns dark and gives a purple solution or suspension, which with the application of the electric current heats and boils and certainly conducts to an appreciable extent.) It may be noted that many of the suspensions in aniline show appreciable cataphoresis. (2) Alcohols, phenols and their salts, aldehydes, ketones, esters and ethers, e.g. phenyl-ethyl-alcohol, β-naphthol, phenol and potassium carbolate, acetone, acetophenone, salol, methyl-benzoate, anethole and ethyl ether. Some of these substances are said to unite with aniline[1]; but the compound- or complex-formation evidently does not give any appreciable conductivity. (3) Free bases, hydrocarbons, organic chlorides, etc., e.g. urea, m- phenylenediamine, quinine, benzene, iodoform and chlorobenzene.

These "non-conducting" solutions are certainly of varying electrical conductivities. Thus the weak acids, like benzoic, camphoric, cinnamic, anthranilic and anisic acids, were included here, though they differ only in degree from the stronger acids that give appreciably conducting solutions. Again, acetanilide is fairly soluble in aniline; its solution was classed as non-conducting; a quantitative measure of its conductivity is given later.

Quantitative Experiments. All the materials were purified and dried and were kept in desiccators throughout. The aniline was kept for long periods over solid caustic potash, and then distilled; only the middle fractions of constant poiling point were used, and these were of pale yellow colour. The electrical conductivities at 30° of the samples of aniline varied from 0.000,000,029 to 0.000,000,020 ohm-cm. units; the former samples are most likely to contain traces of water, the latter to contain higher homologues of aniline. Their densities at 30° varied from 1.01292 to 1.01336. One sample of aniline initially had $k = .0_7206°$ and $D^{30°}_{4°} = 1.01336$; this was 48 days after distillation; when finishing work with this sample 60 days later, i.e. 108 days after distillation, it was found that $k = .0_7273$ and $D^{30°}_{4°} = 1.01332$. Thus in two months the density had scarcely changed and the conductivity had increased by $.0_87$, not an appreciable amount and possibly an extreme value as the other samples of aniline were used up more quickly than this one. This increase of conductivity was probably due to absorption of traces of

[1] Oddo and Tognacchini: J. Chem. Soc., **124 I**, 224 (1923).

water. The electrical conductivities of the solutions, as given in the tables, are all "corrected" for the conductivity of the aniline (solvent); that is, the figures in the tables are the conductivities of the solutions *as found* minus that of the solvent, which latter is shown in the table underneath the figures corrected thereby.

The conductivity measurements were made by the usual Kohlrausch (Wheatstone bridge) method. Wireless head-phones, each of a resistance of 2000 ohms, were found to be better than low-resistance telephones. The resistances of the cells containing the solutions were from 50 to 300,000 ohms, excepting with some extreme cases and with the aniline alone. Two electrolytic cells were used; their "cell-constants" were .1072 and .03415. The latter values were found by standardisation at 30° with N/100 (18°) potassium chloride solution, carefully made from the purified salt and water, and assumed to have at 30° k = 0.001,552 *plus* the *k* of the water, which was 0.000,003. In standardising these cells with this dilute potassium chloride solution care was necessary to avoid bubbles forming on the electrodes; by exhausting the air from the stock bottle of the solution for some time before using, this trouble could be minimised. The average error in the determination of the resistance of a cell full of electrolyte was ±0.32%. The error was somewhat greater when the cell resistance was over 150,000 ohms. It is well known, however, that in this work larger errors may occur between different or duplicate experiments. In the tables there are given with each solute the independent figures of at least two series of experiments. The cells were placed in a thermostat kept within one or two hundredths of a degree of 30°, using a standardised thermometer. While a solution was in the conductivity cell, there was often a slight tendency for the conductivity to increase, say, by 1 to 5 parts in 1000; this may be due to better contact at the electrodes after slight passage of current. When the solutions in aniline had a lower conductivity than 0.000,001, the error of experiment increases, the influence of traces of moisture and of other disturbing impurities becomes greater, and the conductivity of the aniline itself (or the 'blank' which is subtracted from the observed conductivity to give the value quoted) becomes relatively large; for such solutions therefore the total errors are liable to be large.

The mixtures were all made up by weight in well-stoppered weighing bottles, which were kept in desiccators over calcium chloride or sulphuric acid as much as possible. One mixture was made up from solute and solvent; part was used for the determination of the electrical conductivity or density, and the remainder was diluted with further solvent to give a new solution. The parent solutions of a series are denoted in the tables by an asterisk (*) after the percentage of solute. The densities ($30°/4°$) of certain solutions were determined with all precautions, and thus the concentrations in gram-molecules per litre at 30° of all the solutions could be determined, since the density-percentage weight curves for these dilute solutions were practically straight lines.

(1) *Solutions of Acetic Acid in Aniline.*

A study of the density, viscosity and electrical conductivity of mixtures of acetic acid and aniline was completed in this laboratory[1] in 1923; but the whole field of possible mixtures of these substances, with and without water, was then covered. The present work was done with more dilute solutions of the anhydrous liquids. The acetic acid, which had been previously purified, was traced with phosphorus pentoxide, filtered off and distilled, and the middle fraction, B.P. = 119.0-119.5°, was collected. The electrical conductivities of these solutions showed no signs of altering on keeping. The acetic acid concentrations in gram-molecules per litre at 30° were calculated from the percentage weights of acid and from the densities obtained from the 1924 data, from which source we had the following results:—

Densities and Viscosities of Solutions of Acetic Acid in Aniline at 30° in C.G.S. Units:—

% wt. of acid	Density	Viscosity
16.375	1.0284	.0450
8.1905	1.0202	.0366
2.8880	1.0154	.0336
1.6234	1.0144	.0328
0	1.0131	.03226

With monochloracetic acid dissolved in aniline the conductivity of the solution rapidly increased with time; e.g. with a solution of 0.9% monochloracetic acid in aniline the initial specific conductivity at 30° was about 0.000,002, and this more than doubled after 24 hours' keeping at 10°. Thus the solution of such a strong acid in aniline is not in equilibrium. With the above solution, crystals (the anilide?) appeared throughout the mixture after half an hour, but these disappeared after two days and then the solution became red-brown, the colour deepening with time and hydrochloride accumulating in the solution.

(2) *Solutions of Aniline in Acetic Acid.*

The same materials were used as in (1). These mixtures, when first made, had a slight pink colour; this rapidly faded to a straw colour and on further dilution with the acid became colourless. Here with the mixtures containing small percentages of aniline, i.e. with 2% aniline or less, the electrical conductivity decreased with time, the rate of decrease being greater at 30° than at room temperature (10° to 20°), and consequently these results, marked §, are but approximate. In any experiment where the electrical conductivity was found to vary, the initial values are given in the tables. With mixture 39 the conductivity decreased to half the original value after 24 hours at room temperature, 20°, though with mixture 38 no decrease in conductivity was noticed. With mixture 44 the conductivity decreased by 0.35% while the determination was being made, i.e. within 1/4 hour at 30°, and by 22% after 4 hours at 25°. This decrease in conductivity with time is probably connected with the action of the aniline and the acetic acid to form acetanilide and

[1] Pound and Russell: J. Chem. Soc., **125**, 769; Pound: 1560 (1924).

water; this action is faster probably in acetic acid solution than in aniline solution; the acetanilide forms poor conducting solutions in both these solvents (pp. 551, 552). However water is formed at the same time by this condensation, and this would tend to make the solutions better conductors. Thus the change in the conductivity of aniline dissolved in acetic acid will not be simple; and it might happen that the same action, which would produce a decrease in conductivity in dilute solutions, might produce an increase in conductivity in more concentrated solutions. The 1923 results with aniline in acetic acid are higher than these results but parallel to them. The present results are the better, the liquids being purer and drier. It might be noted that the conductivity of the acetic acid more than doubled during the course of the experiments over the period of one month; but the last of these experiments, 42 to 44, were done three weeks after the previous three series. This increase in conductivity is certainly due to the absorption of traces of water. The densities and viscosities of these solutions were taken from the 1923 data, e.g.:—

% wt. Aniline	Density (30°/4°)	Viscosity (30°)
28.693	1.08426	0.1371
21.010	1.08125	———
10.729	1.0661	———
5.259	1.05313	———
0	1.03779	0.01031

(3) *Solutions of Acetic Anhydride in Aniline.*

The acetic anhydride was prepared from May and Baker's "Acetic Anhydride". Sample (1) used in experiments 46 to 51, was obtained by shaking the original with phosphorus pentoxide for some minutes, filtering and distilling. The collected distillate was the last third and had B.P. = 137.0-139.4°; its conductivity at 30° was 0.000,001,77. Sample (2) of acetic anhydride, used in experiments 54 to 58, was obtained by treating May and Baker's liquid with sodium at room temperatures for 48 hours, filtering off from the sodium acetate, shaking with phosphorus pentoxide for some minutes, filtering and distilling. The collected distillate had B.P. = 137.7-139.2°, and its conductivity at 30° was 0.000,002,765. These comparatively high values for the electrical conductivity of the acetic anhydride probably indicate the presence of some acetic acid, even though the second method of purification is supposed to be efficient.[1]

Aniline and acetic anhydride mix with evolution of heat, and the mixtures are good conductors. A mixture of approximately equal volumes of these two liquids is quite viscous when it cools to room temperatures, and from the solution crystals (acetanilide) readily separate. Such a mixture containing 39.42% wt. of acetic anhydride had at 30° the conductivity of 0.000,573 approximately, indicating that the conductivity-composition curve for these mixtures is similar to that for acetic acid-aniline mixtures, where the conductivity rises to a maximum for some mixture of intermediate composition.

[1] Walton and Withrow: J. Chem. Soc., **126** II, 209 (1924).

With dilute solutions of aniline in acetic anhydride the electrical conductivities decrease rapidly with time; e.g. a solution with 5.7% wt. of aniline had a conductivity of 0.000,004,41, and its conductivity decreased by 8% in 1/4 hour at 30°. The acetic anhydride alone had k = 0.000,002,76, so that the initial 'net' conductivity of the solution was 0.000,001,65. Such solutions in a solvent which itself is of high conductivity are unsuited for study. Solutions of acetanilide in acetic anhydride also gave conductivities decreasing with time; e.g. a 10.375% solution of acetanilide in the above acetic anhydride gave k = 0.000,005,46, decreasing by 1.3% in 1/4 hour at 30°; the initial 'net' conductivity is thus 0.000,002,70. Probably aniline in acetic anhydride quickly gives acetanilide and acetic acid, and then more slowly diacetanilide is formed.

With dilute solutions of acetic anhydride in aniline the conductivities do not vary too quickly with the time, and a consistent set of values may be obtained. However the general tendency is for the conductivities of these mixtures to increase with the time; e.g. with mixtures 47, 49, 51 and 58 the conductivities increased by 1.2, 1.5, 6.0 and 27% after 164, 144, 101 and 768 hours' keeping at room temperatures respectively. The rate and the proportional amount of increase of conductivity are the greatest for the most dilute solutions, the last example being the extreme case observed. The probable chemical actions, when the aniline is in excess, are:—

$$\text{Acetic anhydride} + \text{Aniline} \rightarrow \text{Acetic acid} + \text{Acetanilide} \qquad (1)$$

and

$$\text{Acetic acid} + \text{Aniline} \rightarrow \text{Acetanilide} + \text{Water} \qquad (2)$$

Action (2) must be much slower than action (1); thus with solutions of acetic acid in excess of aniline no evidence of change of conductivity was noticed during the experiments, though doubtless it would occur after keeping for days. The tables show that the acetic anhydride gives a better conducting solution with aniline than the acetic acid and acetanilide derived from it would give, adding the conductivities due to the latter substances together; either then the effect of the last two substances together, with or without unchanged acetic anhydride, is not additive, or traces of water from action (2) are rapidly formed, or other actions must be taken into account. Probably additive compounds are first formed between the solvent and solute; and their ionisation determines the initial conductivity, and their subsequent changes the changes of conductivity. Solutions of acetic anhydride in aniline are better conductors than solutions of acetic acid in aniline, comparing either equi-molecular solutions or equivalent solutions above 0.75 normal; below 0.75 normal the solutions of acetic acid are the better conductors. But solutions of phthalic acid are better conductors than equi-molecular solutions of phthalic anhydride in aniline (v. later).

The following densities were obtained for solutions of acetic anhydride, sample (1), in aniline:—

% wt. of acetic anhydride	Density (30°/4°)
anhydride	
9.4506	1.02808
4.9140	1.02099
100	1.06670
0 (Aniline)	1.01292

Also a solution of acetanilide in aniline, containing 4.7363% of acetanilide, had at 30° the (net) specific conductivity of 0.000,000,101.

(4) *Solutions of Phthalic Anhydride in Aniline.*

May and Baker's well-crystallised phthalic anhydride was kept in an exhausted desiccator over sulphuric acid for several days before making the solution in aniline. Solution was effected by gentle warming, say at 50°, except that mixture 68 was prepared in the cold, requiring six days at about 12°. Mixture 68a is about saturated at room temperatures. Aniline and phthalic acid condense and form phthalanilic acid, $Ph.NH.CO.C_6H_4.CO.OH$, then phthalanilide, $(Ph.NH.CO)_2C_6H_4$, and then phthalanil, $PhN\langle^{CO}_{CO}\rangle C_6H_4$; the first compound[1] is formed in twenty minutes at ordinary temperatures. From a solution of phthalic anhydride in aniline, that has been heated to the boiling point, crystals separate on cooling. The various solutions of phthalic anhydride in aniline gave moderately consistent values for their conductivities, which too were unaltered after keeping twelve days at room temperatures. The following densities were determined:—

% Phthalic anhydrate	Density (30°/4°)
4.997	1.03194
0.7305	1.01542
0	1.01292

(5) *Solutions of Phthalic Acid in Aniline.*

Merck's crystalline phthalic acid was dried over calcium chloride and dissolved by gentle warming in the aniline. It did not dissolve readily. Its solubility was small; the solution with 0.5% of phthalic acid slowly became turbid even at 30°. This solution had at 30° the density of 1.01496, while the aniline had density of 1.01321. With solution 77, the conductivity had increased by 1% after keeping for 5 days; in other experiments the increase of conductivity with time was similarly slight.

(6) *Solutions of Phenyl-acetic Acid in Aniline.*

Solutions of well-crystallised phenyl-acetic acid were prepared as with the preceding solids. The 10% solution was about saturated at 13°. The conductivities were low, and they increased with the time of keeping in the cell at 30° by 1% or more in 1/4 hour. The accuracy of the determinations is therefore moderate; the conductivities of mixtures 82 and 83 are higher than those of the others. The solution with 10.034% of phenyl-acetic acid had at 30° the density of 1.02569, while the aniline had the density of 1.01292.

[1] Tingle and Cram: Am. Chem. J., 37, 596 (1907).

(7) *Solutions of Salicylic Acid in Aniline.*

These solutions were made from the dried Merck's pure salicylic acid and aniline by gentle warming. The solubility was low. The conductivities were low, and increased somewhat with time—similar to those of the phenyl-acetic acid solutions. The mixture 89 was kept in the desiccator at room temperatures for 11 days before determining its conductivity, but the result seems quite a normal one. The densities of these dilute solutions were assumed from those of similar dilute solutions of phenyl-acetic acid and benzoic acid.

(8) *Solutions of Benzoic Acid in Aniline.*

Howard's sublimed benzoic acid was dried in an exhausted desiccator over sulphuric acid for several days. The solutions were usually made with the aid of gentle warming. Mixture 141 was made in the cold (12°) from the same benzoic acid after resubliming; it took 4 days to dissolve. The mixtures containing much benzoic acid, say 10% and over, were appreciably more viscous than the original aniline. The mixture with 18% benzoic acid solidified on standing at 10°; the crystals were probably some aniline benzoate.[1] The following densities were determined:—

% benzoic acid	Density (30°/4°)
14.888	1.03685
8.676	1.02677
5.0515	1.02100
1.988	1.01625
0	1.01315

The ready solubility of benzoic acid in aniline permits the examination of many mixtures, but unfortunately the electrical conductivities are so low that the experimental errors and the influence of probable impurities, say the slightest traces of water, are large. The lowest results—presumably the most accurate—are those with mixture 141 (v. above) and mixture 142, which was made by diluting the former with aniline. Mixtures 100 to 104 gave higher conductivities which were neglected.

(9) *Solutions of Aniline Hydrochloride in Aniline.*

Aniline sulphate is not at all soluble even in boiling aniline, and the solution does not conduct appreciably; the concentration of the dissolved salt is probably less than 0.05%. Aniline hydrochloride, however, is appreciably soluble in aniline; the mixture 135 with 6.38% of aniline-hydrochloride solidified entirely on keeping for an hour or so at 13°; the solid may be some compound[2] like 2 An., HCl. The solutions of aniline hydrochloride in aniline are relatively good conductors. There was little or no tendency for the conductivity of these solutions to vary with time; e.g. after 8 days the conductivity of mixture 134, $k \times 10^6 = 17.55$, had decreased by less than 0.4%, though the mixture had become a little darker in colour. Merck's pure aniline hydrochloride was used after drying in an desiccator over sulphuric acid for several

[1] Berthelot: J. Chem. Soc., 53, 1361 (1890).
[2] Mandal: J. Chem. Soc., 120 I, 106 (1921).

days. Mixture 133 was made in two days at room temperature, about 20°, but the other parent mixtures were made by gentle warming. The following densities were found:—

% wt. of aniline hydrochloride	Density (30°/4°)
6.3836	1.02527
4.3978	1.02159
0.8205	1.01475
0.2690	1.01366
0	1.01300

Mixtures 133 and 134 gave higher conductivities than the others and are not quoted in the tables. Mixtures 135 to 140, the third series, tend to have lower conductivities than the mixtures of the first two series and are probably the most accurate. The concentration of the aniline hydrochloride in gram-molecules per litre is, of course, also the concentration of hydrochloric acid, assuming that the acid were dissolved in the aniline and subsequently combined with it. Subsequently we shall often refer to these solutions as solutions of hydrochloric acid in aniline.

(10) *Solutions of Saccharin in Aniline.*

Saccharin, o-sulpho-benzimide, is easily soluble in warm aniline, and the solutions are relatively good conductors. The best commercial saccharin was dried in an exhausted desiccator over sulphuric acid, and the solutions were made by gentle warming. Saccharin from two different sources was used with no difference in the results; e.g. mixtures 105 to 108, 120, and 121 to 124 were made with sample (1) saccharin; mixtures 113 to 119 were made with this saccharin after sublimation; mixtures 109 to 111 were made with sample (2) saccharin. The parent mixtures 113, 120 and 121 were made in the cold within 24 hours. The conductivities of mixtures 113 and its derivatives were slightly higher than those of the other mixtures; this may be due to the sublimed saccharin being the purest. The mixtures tend to become browner on keeping. Mixtures 105 to 111 were done with one sample of aniline, and mixtures 113 to 124 with another. The conductivities of these mixtures decreased very slightly with time, e.g. the conductivity of 108 decreased by 1% after 6 days. Mixture 116 was made from 114 after a lapse of 11 days. The following densities were determined:—

% wt. of Saccharin	Density (30°/4°)
8.2631	1.04760
7.9571	1.04611
6.2058	1.03884
5.0571	1.03398
2.5663	1.02375
0	1.01320

Discussion of the Results

Here we refer to the concentrations of the solutes, c, in gram-molecules per litre at 30°, the specific conductivities, k, in ohm- cm. units, and the molecular conductivities, A or k/c. The specific conductivity-concentration curves, k-c curves, Fig. 1, are in general concave to the k axis, and their

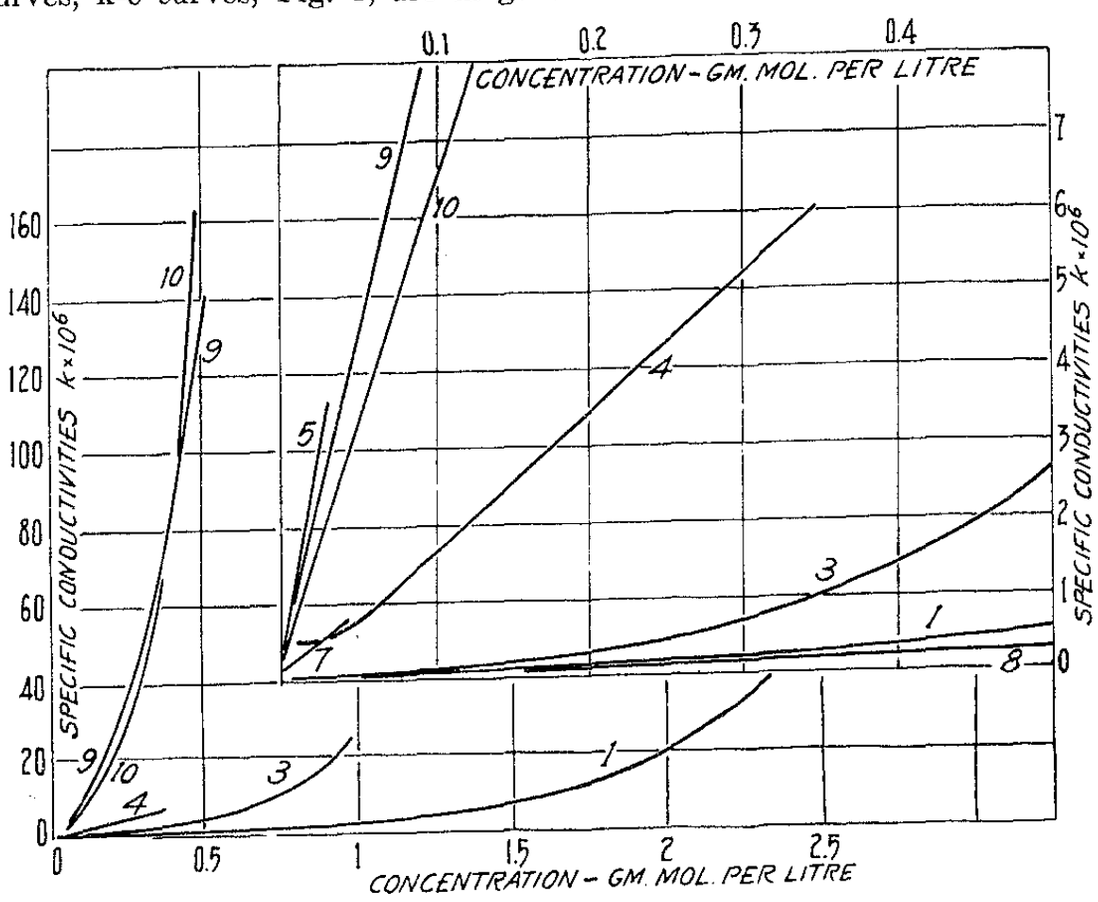


FIG. 1

'steepness' increases with c. Of course, with completely miscible solutes, like acetic acid in aniline, at high concentrations the curve has a point of inflexion, bends and reaches a maximum, and thence descends towards the c-axis once more; but we are not concerned with these concentrated solutions here. With our dilute solutions the k-c curves are, in general, concave towards the k-axis throughout, and so that for a certain range of concentration k is, with more or less accuracy, proportional to c, then for a higher range of concentrations proportional to c^2, then to c^3, and so on. At low concentrations, c = 0 to 0.1 approximately, we have $k \propto c$, or the k-c graph a straight line, for saccharin, hydrochloric acid (aniline hydrochloride), phthalic acid, phthalic anhydride and salicylic acid in aniline. The k-c straight lines for these solutions do not go through the origin (O,O), but at zero concentration indicate $k \times 10^6 = 0.3$ approximately. However the behaviour in extremely dilute solutions must be determined by more accurate experiments. With the other five solutions the curve is concave throughout and also apparently goes to the origin. The k-c curve probably goes to the origin for salicylic and phthalic acids also. The k-c curves for the last two substances show a resemblance to the k-c

curves for solutions of electrolytes in water (v. later). In general the k-c curves do not cross. The order of the curves for the solutions in aniline is as follows, proceeding from the solutions of lowest to those of highest conductivity:—Benzoic acid, phenylacetic acid, acetic acid, acetic anhydride, phthalic anhydride, salicylic acid, saccharin, hydrochloric acid (aniline hydrochloride), and phthalic acid. Comparative values for the specific conductivities are given below. (The curves for hydrochloric acid and saccharin cross at c = 0.3; and the phthalic anhydride curve at low concentrations cuts the salicylic acid curve, but this part of the phthalic acid curve is perhaps abnormal.)

Specific conductivities, k × 10^6, for solutions

Gm. mol. per litre	Acetic acid in aniline	Aniline in acetic acid	Aniline solutions of Acetic anhydride	Aniline solutions of phthalic anhydride	Phthalic acid
('	1	2	3	4	5
.025	(.01)	——	(.013)	(.55)	3.17
.05	(.03)	——	(.031)	.68	——
.1	(.05)	.5?	(.081)	1.58	——
.5	.52	252	2.55	(8.6	——
1.0	2.22	1430	26.4	——	——

	Aniline solutions of Phenyl. acetic acid	Salicylic acid	Benzoic acid	Hydrochloric acid	Saccharin
('	6	7	8	9	10
.025	(.01)	.48	——	2.4	1.7
.05	(.03)	(.86)	——	4.2	3.1
.1	(.05)	——	.065	9.3	7.1
.5	.386	——	.20	138	180
1.0	——	——	.52	——	——

Values in brackets are extrapolated.

Tables

Specific electrical conductivities, k, and molecular conductivities, A = k/c, of solutions at 30° containing w% weight of solute and of concentration, c gram-molecules of solute per litre at 30°.

Number of Experiment	% wt. of Solute w	Concentration c	Specific Conductivity k × 10^3	Molecular Conductivity A × 10^6
(1) Solutions of Acetic Acid in Aniline ($C_2H_4O_2$; mol. wt. = 60.03):—				
24*	16.375	2.8047	99.27	35.38
25	8.1905	1.3917	5.804	4.173
26	2.8880	0.4884	0.5095	1.043
27	1.6234	0.2743	0.1884	0.6866
28*	12.763	2.1787	30.19	13.86
29	8.2317	1.3987	5.850	4.181
30	5.3841	0.9126	1.8467	2.023
31	3.3912	0.5738	0.6908	1.2045
32	1.5955	0.2696	0.1835	0.6806
	0	0	0.0288	

TABLES (Contd.)

No.	w	c	k × 10^6	A × 10^6
(2) Solutions of Aniline in Acetic Acid ($C_6H_5 . NM_2$; Mol. Wt. = 93.06):—				
33*	14.684	1.695	2931	1730
34	9.840	1.125	1753	1558
35	6.126	0.6958	635.4	913.5
36*	9.0685	1.0355	1539	1486
37	4.890	0.5549	344.2	621.5
38	2.636	0.2963	46.30	156.2
39	1.421	0.1592	(>) 0.30§	1.9
40*	4.2455	0.4795	222.1	463.1
41	2.0105	0.2254	17.37	72.05
	0	0	0.082	
42*	2.0676	0.2319	19.55	84.35
43	1.0205	0.1142	0.522§	4.57
44	0.5446	0.06086	0.217§	3.57
	0	0	0.193	

Notes: *, after the number of an experiment, denotes that this was a parent mixture, i.e. the mixture was made up from solute and solvent directly, and from which the following mixtures were made by dilution with solvent.
§ indicates that the conductivity was decreasing with time.
" " " " " increasing " " .

(3) Solutions of Acetic Anhydride in Aniline, $(CH_3 . CO)_2O$; Mol. Wt. = 102.05:—				
46*	13.156	———	74.74	———
47	7.5495	0.7580	9.836"	12.97
48*	5.907	.5915	4.311	7.286
49	3.2565	.3246	0.807"	2.488
50*	2.7580	.2748	0.547"	1.991
51	1.5018	.1495	0.1554"	1.039
54*	9.663	.9740	23.79	24.42
55	5.4046	.5410	3.308"	6.115
56	2.968	.2958	0.647"	2.189
57*	2.360	.2350	0.3830	1.630
58	1.2472	.1239	0.1100"	0.888
	0	0	0.0215	
(4) Solutions of Phthalic Anhydride in Aniline; $C_8H_4O_3$; Mol. Wt. = 148.03:—				
63*	3.139	0.21705	3.875	17.85
64	1.810	.12455	1.968"	15.80
65	0.9684	.06645	1.072"	16.13
66*	0.9574	.06573	1.068"	16.25
67	0.3849	.02637	0.537"	20.37
68*	0.7305	.05015	0.6890	13.74
68a*	4.997	.3484	6.061	17.39
	0	0	0.025	

TABLES (Contd.)

No.	w	c	k × 10⁷	A × 10⁶
(5) Solutions of Phthalic Acid in Aniline; $C_8H_6O_4$; Mol. Wt. = 166.05:—				
72*	0.4985	0.03044	3.647	119.8
73	0.2600	.01587	2.122	133.8
76	0.12895	.007872	1.203	152.9
77	0.06935	.004231	0.785″	185.6
75*	0.3038	.01855	2.396	129.1
78	0.1530	.009340	1.350	144.55
79	0.07635	.004660	0.8233	176.7
80	0.04104	.002505	0.5577″	222.7
81	0.01734	.001058	0.3278″	309.9
	0	0	0.0275	
(6) Solutions of Phenyl-acetic Acid in Aniline; $C_6H_5 . CH_2 . CO_2 . H$; Mol. Wt. = 136.06.				
69*	10.034	0.7570	0.703″	0.9285
70	6.004	.4506	0.327″	0.726
71*	3.036	.2270	0.1343	0.592
	0	0	0.0248	
82*	3.659	0.2739	0.179″	0.650
83	1.629	.1216	0.0704″	0.579
	0	0	0.0275	
(7) Solutions of Salicylic Acid in Aniline; C_6H_4 (OH) (COOH); Mol. Wt. = 138.05.				
85*	0.4506	0.03309	0.6005″	18.15
86	0.2516	.01847	0.393	21.3
87	0.1217	.008936	0.246	27.55
88*	0.5755	.04226	0.729″	17.25
89	0.1837	.01348	0.319	23.7
90*	0.3870	.02841	0.535″	18.85
91	0.07275	.005340	0.178	33.3
	0	0	0.022	
(8) Solutions of Benzoic Acid in Aniline; $C_6H_5 . COOH$; Mol. Wt. = 122.05.				
92*	1.9882	0.1655	0.0951	0.5745
93*	8.6760	0.7300	0.3595″	0.4925
94*	5.0515	0.4228	0.195c	0.4612
95*	14.888	1.265	0.7344	0.5805
96	5.1114	0.4349	0.2230″	0.5126
97	2.6944	0.2248	0.1087″	0.4839
98*	18.156	1.5505	1.010	0.6517
99	11.224	0.9488	0.4920	0.5183
	0	0	0.0222	
141*	7.035	0.5900	0.2522	0.4275
142	3.1768	0.2650	0.1097	0.4140
	0	0	0.0235	

TABLES (Contd.)

No.	w	c	k × 10^6	A × 10^5
(9) Solutions of Aniline Hydrochloride in Aniline; C_6H_7N. HCl; Mol. Wt. = 129.53.				
125*	5.524	0.4369	109.63	251.1
126	2.1382	0.1680	20.20	120.2
127	0.8205	0.06425	5.882	91.6
128	0.2690	0.02104	2.160	102.6
129*	4.3978	0.3470	71.37	205.7
130	1.2742	.1000	9.818	98.2
131	0.5329	.04173	3.827	91.7
132	0.2035	.01593	1.856	116.5
	0	0	0.020	
135*	6.3836	0.5054	141.0	279.0
136	3.5629	0.2808	45.30	161.3
137	1.8240	0.1432	15.07	105.2
138	0.9937	0.07783	6.879	88.4
139	0.3820	0.02990	2.696	90.2
140	0.1381	0.01081	1.269	117.4
	0	0	0.023	
(10) Solutions of Saccharin in Aniline; $C_7H_5O_3NS$; Mol. Wt. = 183.11.				
105*	7.9571	0.4543	132.03	290.6
106	5.0571	.2857	45.77	160.3
107	2.5663	.1435	12.42	86.6
108	1.2848	.07146	4.674	65.4
109*	5.0942	.2875	44.31	154.1
110	2.8995	.16245	14.33	88.2
111	1.0579	.05881	3.674	62.5
	0	0	0.020	
113*	8.2631	0.4727	164.5	348.0
114	2.9939	.16775	17.22	102.6
116	1.4644	.08154	5.283	64.8
117	0.7458	.04136	2.528	61.1
118	0.3311	.01832	1.291	70.5
119	0.06616	.00366	0.4525	123.6
120*	1.0103	.05616	3.694	65.8
121*	1.4094	.07843	5.461	69.6
122	0.6468	.03590	2.367	65.9
123	0.2597	.01437	1.153	80.3
124	0.10405	.005756	0.6325	109.9
	0	0	0.020	

In general, the molecular conductivity, A, rises increasingly rapidly with increasing concentration. At low concentrations, c = .05 to .1, A often reaches a minimum, and then at lower concentrations A rises with decreasing

concentration; such is the case with the aniline hydrochloride and saccharin solutions. With phthalic and salicylic acids we can deal only with low concentrations, and here throughout the A-c curves fall with increasing concentration. Thus with these two acids dissolved in aniline we have an approach to the behaviour of weak electrolytes, like acetic acid, in aqueous solutions. There is, however, no definite limiting molecular conductivity at zero concentration, as the A-c curve is asymptotic to the A-axis. For the curves that rise to some value of A_o, however indefinite, at zero concentration we have the following more or less probable values of A:—phthalic acid, 400-600; saccharin, 160; hydrochloric acid, 160; salicylic acid, 50. With phthalic anhydride and benzoic acid the A-c curve is doubtful at low concentrations; the experimental errors are here too large. With the other solutions the A-c curve, in the absence of more accurate data, falls throughout to the limiting values,—for acetic acid, 0.35; acetic anhydride, 0.5; phenylacetic acid, 0.45; and for aniline in acetic acid probably zero. In these solutions, for which A falls with decreasing concentration, the nature of the ionisation, etc., must be vastly different from the conditions holding in aqueous solutions. Also in the former solutions the significance of A_o, if it is other than zero, must be different from that usually accepted for A_o in aqueous solutions, where the maximum value, A_o, is held to indicate complete ionisation.

We endeavoured to see whether the mass-action law held for these solutions. If we suppose a binary electrolyte, ionising as $AB \leftrightarrows A^+ + B^-$, and let c = the concentration of the original electrolyte AB and γ = the degree of ionisation, then if the mass-action law holds $k_1c(1 - \gamma) = k_2c^2\gamma^2$. In the usual consideration of aqueous solutions we put $\gamma = A/A_o$, and deduce that $1/A = (1/aA^2_o)(CA) + 1/A_o$, where a = the ionisation constant $= k_1/k_2$; whence 1/A is a linear function of (CA) or k (the specific conductivity). It is, however, not necessary to consider the value of A_o in order to test this relationship. For k is proportional to c, the ion concentration, or $\gamma = k/dc$, where d is a constant; then the mass-action equation leads to $\frac{k^2}{d(dc - k)} =$ the ionisation constant, a; whence $\frac{c}{k} = \frac{1}{ad^2}k + \frac{1}{d}$, which is the same relation as found before. It is necessary to note this, for in the present solutions the functions A_o and A/A_o have little or no significance. We have tested the agreement of our data with this equation. We find that for aniline in acetic acid and for acetic acid, acetic anhydride and phenylacetic acid in aniline the c/k—k curve is hyperbolic and asymptotic to both axes. For phthalic and salicylic acids in aniline this curve is concave to the k-axis and approaches the c/k axis asymptotically; probably here the mass-action law holds approximately for very dilute solutions. With hydrochloric acid and saccharin in aniline the curve is a compound of the above types; as k decreases, c/k rises till it reaches a maximum value, after which it decreases again as for phthalic acid. For our solutions the mass-action law holds, if at all, over a very low range of concentrations indeed.

We then tested the applicability of the Kraus and Bray equation for electrolytes where the ionisation is low, i.e. $cA^2 = P(cA)^m$ or $k^2/c = Pk^m$, where P and m are constants.[1] From this equation we have $\log k^2/c = m. \log k + \log P$. For hydrochloric acid in aniline and for aniline in acetic acid we found that the graph of $\log (k^2/c)$ against $\log k$ was roughly a straight line. But on working back from this line to values of k from given values of c, we found that the calculated values agreed only approximately with the observed values. For example, with aniline in acetic acid the constants were $m = 1.635$ and $P = 14.45$, and the average deviation of the calculated values of k from the observed values of k was -4%; the Kraus and Bray equation was only an average equation over the range $c = 1.1$ to 0.2. Similar results held for solutions of hydrochloric acid in aniline. Quite as good results may be obtained from a relation like $k = x(y - c)^n$, where x, y and n are constants; or, for example, for most of our solutions of hydrochloric acid in aniline by the equation $k = 538\ c^2 - 4$, over the range of $c = 0.5$ to 0.1. The plotting of complex functions, especially those involving logarithms, is liable to become quite misleading, if the errors introduced in obtaining those functions (and logarithms) are not allowed for.

The Kraus and Bray relationship reduces to $k^{2-m} = p.c$, or $k = q.c^p$, where q and p are constants, and thus $\log k = p. \log c + \log q$. It is simpler to try the graph log k-log c than the graph of $\log (k^2/c)$-log k. For none of our solutions in this graph log k-log c a straight line over the whole range of the experiments, except perhaps for phthalic anhydride, for which substances however the results are not of the highest accuracy. For the aniline solutions of phthalic and salicylic acids and perhaps of acetic anhydride, the log k-log c graph is a straight line over a range of the lowest concentrations; over these concentrations therefore the Kraus-Bray modified equation holds. In general the log k-log c curves are concave to the log k axis, i.e. log k increases faster than log c; for solutions of aniline in acetic acid the reverse holds.

It is clear that the relations between k and c for various electrolytic solutions are not covered by any simple extensions of the law of mass-action for any considerable ranges of concentrations. We may write provisionally that $k = q.\ c^p$, where q is a constant and p is some function of c. If the form of the function p is the same for all electrolytes, then the constants there involved must alter greatly. For solutions of salts in water, $p < 1$, and the k/c curve approaches the zero asymptotically to the k-axis; and for many non-aqueous solutions $p > 1$, and the k/c curve approaches zero asymptotically to the c-axis. Even then one such equation can only hold for one electrolyte from zero to moderate concentrations, as a k/c curve usually exhibits a maximum at a certain value of c. The connection between k and c must indeed involve the reasons for ionisation and the relations between the ions and the solvent and the relations between the ions themselves.

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[1] Kraus: loc. cit., p. 75.
[2] Kraus: loc. cit., p. 79.

Summary

Solutions in aniline are relatively poor conductors of electricity. The conducting solutions behave generally like typical non-aqueous electrolytic solutions.

Thus the specific conductivities rise so rapidly with increasing concentration of solute, that the molecular conductivities also rise rapidly with increasing concentrations.

No simple equation was found to express the relations between the specific conductivity, k, and the concentration of solute, c. Evidently $k \propto q.c^p$, where p, at least, is some function of c.

At very low concentrations some solutions in aniline behave like aqueous solutions and the molecular conductivity rises to a limit at zero concentration; more delicate experiments might extend the number of these solutions.

The stronger acids with aniline give solutions of which the conductivities tend to increase with the time. Assuming the initial conductivity is due to the formation of aniline salt, the subsequent formation of aniline and liberation of water will explain the increase of conductivity.

The School of Mines,
Ballarat,
Victoria,
Australia

January 24, 1924.

ON THE NATURE OF THE INFLUENCE OF HUMIDITY CHANGES UPON THE COMPOSITION OF BUILDING MATERIALS*

BY JAMES W. McBAIN AND JOHN FERGUSON

Of all the fluctuating mechanical strains set up in building materials by varying influences, those due to fluctuating humidity are often five times greater than those due to the factor next in importance. The object of the present paper is to isolate this one factor and to investigate its precise nature.

To avoid misunderstanding it must be clearly stated that humidity change is only one factor in the decay of building materials. Hence when we proceed to point out as one of our definite results that certain building materials are wholly exempt from the operation of this factor, it is not to be forgotten that some of the stones may be especially liable to attack by other causes, such as chemical action of the sulphuric acid derived in surprising quantity from the air of towns.

Since there was no information extant as to the amount of water actually taken up by building stones under varying conditions of humidity, we have conducted a systematic series of measurements of the sorption of water vapour by typical materials, ranging from pure crystalline quartz to bricks, sandstones and limestones. It was then shown that parallel results are obtainable by the much quicker method of treatment with dyes such as methylene blue Further insight into the phenomena involved is obtained by sorption experiments with vapours of organic solvents. The results are in accordance with the conception of micellar linkage which has been used in this laboratory in the explanation of the phenomena presented by jellies, soap solutions, detergent action and the viscosity of nitrocotton.[1] Hence we have suggested a highly tentative definition of a stone preservative.

Sorption of Water Vapour

Experimental Method.

The sorption balance of McBain and Bakr[2] was used. This consists essentially in suspending the substance to be investigated in the pan of a delicate spring balance made of fused silica fibre and observing the increase in weight when the substance is exposed to vapour (in this case water vapour) under varying conditions of temperature and pressure.

Fig. 1 shows a sorption tube set up ready for experiment. In use the upper portion of each tube is in an electrically heated air oven while the bottom part is in a water thermostat provided with a thermometer and stirrer, and a large number of tubes are set up side by side. The small portions of the tubes between the oven and the thermostat were heated by a wire coil.

*The work described was carried out for the Building Research Station of the Department of Scientific and Industrial Research and this note is communicated by permission of the department. Crown copyright reserved in Great Britain.

[1] See, for example, J. Phys. Chem., **30**, 239 (1926).

[2] J. Am. Chem. Soc., **48**, 690 (1926).

In Fig. 1 the silica spring S is suspended in the glass tube G from a hook projecting from the glass bulb B which is prevented from slipping down the tube by means of a slight constriction in the tube C. A small bucket made of gold or platinum foil is suspended from a hook at the bottom of the spring. The bucket contains a small weighed quantity of the material under investigation (sandstone, limestone, cement, etc.). In the bottom of the tube, there is placed a small bulb W, almost completely full of water. The bulb is enclosed in a small test tube H, sealed off at the top, and having a small hole A blown in the bottom.

In setting up an experiment the bulb B, with the spring and the bucket suspended from it, is slipped down into the tube T until it rests on the constriction, the water bulb W having been previously placed in the bottom of the tube. The tube is then sealed off at the top K in the blow-pipe flame, and the narrow outlet tube X sealed to a high-vacuum air-pump. The tube is then evacuated until the interior pressure falls below 0.001 mm. During the evacuation the upper part of the tube containing the bucket is heated to 200° C by means of an electric oven, consisting of several turns of nichrome resistance wire wound on a wide glass tube, which slips over the sorption tube. When the pressure has fallen to the required value, the sorption tube is sealed off at a constriction in the narrow outlet tube X.

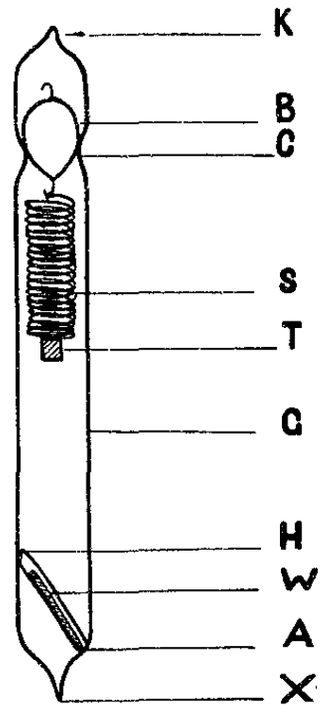


FIG. 1

The tube is now supported in a vertical position, and the length of the spring read by means of a tele-microscope. The extension can be read by means of a vernier to 0.002 cm., corresponding usually to about 0.0001 gm.

The bottom of the tube containing the water bulb is now immersed in a freezing mixture of ice and water, or of carbon dioxide snow and ether. The water in the bulb freezes and in expanding breaks the bulb, so that water vapour is now admitted to the interior of the tube. It is necessary for this process that the water bulb be contained in the shielding test tube H, since particles of glass and ice are thrown violently about the interior of the tube when the bulb bursts, perhaps smashing the spring or capsizing the bucket.

The sorption tube is now supported vertically, with the upper part containing the bucket and spring in the electrically heated oven, and the lower part containing liquid water dipping into the thermostat at a lower temperature. The tubes are observed through a glass window, which is usually kept covered by insulating doors.

On the admission of water vapour to the interior of the evacuated tube by freezing the water bulb as just described, the substance in the bucket immediately begins to take up water from the vapour phase; since the spring has

previously been calibrated, the increase of weight per unit extension length is known. Hence, by measuring the length of the spring, the amount of sorption is deducible to about 0.1 mg.

If the temperature of the upper thermostat is kept at a constant value, 50°C, while the temperature of the lower one is varied from 0° to 50°C, the behaviour of the material in the bucket can be investigated in atmospheres of differing degrees of humidity. The relative humidity is the ratio of the vapour pressures of water at the temperatures of the lower thermostat and of the bucket respectively.

By continuing this procedure at suitable temperatures, the relation between temperature and sorption at constant humidity may be studied, and also the relation between temperature and sorption at constant pressure.

The silica springs are made by coiling a long fibre of silica round a cylindrical carbon rod as described by McBain and Bakr (loc. cit.). The springs used extended about 1/10 mm. for an added load of one milligramme. In a few cases, springs three times as sensitive as this were used. Since an increase in length of the spring could be read with certainty to within 0.02 mm. an increase in weight of 1/15 of a milligram is detectable using the latter spring.

The maximum load which can be safely used on a spring of the first type is 0.5 gm. As the bucket weighs usually 0.1 gm., 0.4 gm of material is the maximum amount employed in these experiments. Usually not more than 0.3 gm. was used. Therefore with the ordinary type of spring, increases in the weight of the material could be read to 1/15% of the total weight.

Each spring was calibrated before use, by measuring its length under various loads. The calibration was carried out at several temperatures as the length of the spring, and the extension per unit length, decrease slightly with rising temperature, since the rigidity modulus of silica has a slight positive temperature coefficient. For this purpose a cylindrical glass oven, wound with several coils of nichrome is employed, inside which the spring is suspended. The oven is connected in series with a rheostat to the electric supply. The temperatures used were usually room temperature, 50°, 100° and 300°C.

Materials studied.

I. *Miscellaneous siliceous materials.*

1) Clear quartz crystal powdered.

2) Leighton Buzzard Sand.

3) Fibres of fused silica (average diameter = 0.004 cm.).

4) Kieselguhr (natural diatomaceous earth).

5) Filter cel ("treated" diatomaceous earth).

6) Gatton stone. This is a stone containing a very large amount (up to 40%) colloidal silica. It has been used as a building stone, but its use is now given up, owing to enormous disintegration on weathering.

Analysis:—	%
Loss on ignition	13.52 (7.8 CO_2)
SiO_2	66.88
Fe_2O_3	2.08
Al_2O_3	2.56
CaO	10.18 (17.7 $CaCO_3$)
MgO	0.11
SO_3	0.19
Alkalies (by difference)	4.48
	100.00

Crystalline silica	25.8%
Combined silica over	5.0%
Remainder (36%) colloidal silica.	

Most of the lime is present as carbonate, though a little $CaSO_4$ is present too. The aluminium and iron will be present as silicates.

II. *Sandstones.*

7) Millstone grit (Idle Quarry).

Analysis:—	%
Loss on ignition	2.24 (H_2O, CO_2 & organic)
SiO_2	85.79
Fe_2O_3	1.68
Al_2O_3	7.00
TiO_2	0.24
CaO	0.52
MgO	0.22
SO_3	0.48
P_2O_5	0.05
K_2O, Na_2O	1.80
	100.02

Traces of Cl, Mn, SnO_2, BaO, F and free V_2O_5 were absent. The CO_2 and organic matter are very low and the composition is very close to that from Darley Dale, (vide infra), which consists of sand grains with orthoclase cemented with siliceous material. The same amounts of sulphates and carbonates occur as in the Darley Dale specimen.

Water absorption 2.5%

8) Millstone grit (Darley Dale). (Stancliffe Stone)

Traces of V_2O_5, SrO, BaO and F were absent. The stone consists of quartz grains with some orthoclase and a siliceous cementing material. Very small amounts of calcium phosphate and sulphate also magnesium and calcium carbonates are present.

Both these grits (7 & 8) are hard compact sandstones. They are fairly resistant to weather, but show movement, with changing moisture content.

Analysis:—	%
Loss on ignition	1.32 (H_2O, CO_2, organic)
SiO_2	87.05
Fe_2O_3	2.08
Al_2O_3	5.85
TiO_2	0.35
CaO_2	0.32
MgO	0.24
SO_3	0.54
P_2O_5	0.04
Na_2O	0.78
K_2O	1.82
Cl	Trace
Mn	Trace
	100.39

Water absorption 6%

9) Kentish Rag.

A cretaceous limestone. The stone is fairly resistant to weather.

Analysis:—	%
Loss on ignition	29.20 (Co_2 27.2)
Total SiO_2	32.15
Fe_2O_3	1.80
Al_2O_3	0.50
CaO	35.50
MgO	0.35
SO_3	0.55
	100.05%

Water absorption 1.7%

The stone contains 61.8% $CaCO_3$, with $CaSO_4.MgCO_3$, and aluminium silicate etc. Most of the silica is present as crystalline silica, not more than 2% being combined.

10) Portland stone.

An oolitic limestone,

Analysis:—	%
Total silica	2.00
Crystalline silica	0.70

Water absorption 4.5%

11) Monk's Park stone.

An oolitic limestone.

Total SiO_2	0.36%

12) Dolomitic limestone (Gold Coast)

Composed chiefly of calcium and magnesium carbonates in molecular proportion.

Total SiO_2	3.26%
Crystalline SiO_2	1.21%
Water absorption	3.6 %

13) Chalk (Setch, Norfolk).

Total silica	3.82%
Crystalline silica	over 0.10%

This is a typical English chalk. They contain usually 90-95% $CaCO_3$ with varying amounts of SiO_2, $MgCO_3$, Fe_2O_3 and Al_2O_3.

14) Stoneycombe stone.

This is almost entirely calcium carbonate similar to a marble.

Total SiO_2	0.46%

15) Buxton limestone.

One of the purest forms of limestone in the world, almost entirely $CaCO_3$.

Total SiO_2	1.00%
Crystalline SiO_2	0.35%
Water absorption	2%

16) Sand-lime brick.

Analysis:—	%
Loss on ignition	6.04
SiO_2	82.62
Fe_2O_3	1.80
Al_2O_3	3.04
CaO	5.60
MgO	0.25
SO_3	0.21
Alkalies	0.60
	100.26
Combined silica	0.70%
$CaSO_4$	0.36%
$CaCO_3$	0.74%

Sand-lime bricks are made from slaked lime and sand, the pressure and moisture being supplied by superheated steam in containers. The proportions are about $7\frac{1}{2}$ parts quicklime to 100 parts of sand by weight, or one volume slaked lime powder to five volumes of sand.

17) Red rubber brick.

This is a soft brick intended to be cut or rubbed down. It is characterised by homogeneity of texture. The burning temperature is fairly high but not so high as, for example, blue Stafford brick.

18) Red wire-cut brick.

These bricks are made from clay in which iron is fairly plentiful say (5-8%).

19) Blue wire-cut brick.

Similar in composition etc. to blue Stafford (see no. 20.) The blue bricks appear to be peculiar to the Midlands as the clay must have a rather high iron content.

Water absorption	4%

20) Blue Stafford brick.

These, like the other blue bricks are a heavy compact form capable of standing high pressures. The water absorption is low, the bricks being

amongst those most impervious to water. The clay is normal in most ways, except for the high iron content, 8-10% usually, as the colour is due to the transformation of the oxide to the protoxide at the very high temperature to which they are burned. The period of burning is also longer than that with most others.

21) Fletton brick.

Fletton bricks are made from lower Oxford clay rich in deposits of marine and vegetable life. It is of the nature of a shale. The bricks are made under great pressure (120 tons per brick area) and are burned at about 1100°C.

Water absorption 20%

22) Stock brick.

This type is a hard burned brick, usually containing blemishes. The clays used vary considerably, the bricks being produced in many localities.

Water absorption 20%

23) Granite. (Meldon).

The sample used was a Dartmoor granite from Devonshire and the composition is usually richer in potash felspar than most granite. It is softer than many other types. Granites are essentially composed of quartz felspar and mica, the *total* silica,[1] being from 60% to 80%.

Sampling of materials.

The building materials were usually supplied in the form of small blocks or as small chunks. These were broken down into pieces about half an inch in diameter, and several of these were ground down in an agate mortar to a fairly fine powder. This was then thoroughly mixed and small portions, 0.2 to 0.3 gm. in weight, taken as the experimental material.

Numerical results.

All the measurements detailed in the following Table were carried out with the sample of material at a temperature of approximately 50° except where otherwise stated. Under the heading x/m × 1000 is given the weight of water in milligrams, taken up from the vapour phase, by one gram of material. The results are in chronological order, and to save space the data in the first four columns are continued in the last four columns. In all cases at least one day elapsed between successive readings.

Sorption is very rapidly completed. It has often been observed, on setting the microscope on the bottom of the spring within one hour of adjusting the temperatures, and then leaving for 24 hours, that the spring point was still at the cross-wire intersection. True equilibrium was attained as is proven (neglecting Gatton stone and Kieselguhr which show hysteresis) by the agreement between values for increasing and decreasing humidity.

[1] The term crystalline silica in the analyses refers to compact uncombined crystalline forms and does not include any which is of a colloidal or absorbent nature which might also be present uncombined. The method adopted for estimating this crystalline silica depended on the far greater reactivity of silica liberated from combination and would include any free colloidal or "soluble" silica with the combined. As the silica in different silicates is liberated, with varying ease, a uniform method is difficult to devise and each case has been treated according to its known composition. The amounts of silicas as given are therefore only to be considered as tentative.

Experiments were carried out in independent duplicates only with Chalk, Dolomitic Limestone, and Millstone Grit, but further isolated points obtained with Millstone Grit and Sandstone fell upon the previous curves.

TABLE I

Temperature Upper	Temperature Lower	Relative humidity	x/m × 1000	Temperature Upper	Temperature Lower	Relative humidity	x/m × 1000
			Sandstone				
56.5°	25.0°	0.19	3.6	49.0°	23.4°	0.25	4.4
50.0	30.0	0.48	4.7	49.2	23.2	0.24	4.3
50.0	36.2	0.48	5.2	50.0	0.0	0.05	1.8
50.0	43.5	0.72	8.5	50.0	22.0	0.21	4.9
48.0	46.1	0.91	9.3	49.2	28.8	0.34	5.7
48.2	48.0	0.99	10.3	49.7	40.3	0.62	7.2
47.2	40.2	0.70	7.5	50.0	45.5	0.80	8.3
47.0	40.0	0.70	7.5	49.0	44.0	0.78	8.0
48.1	35.0	0.50	6.7	30.0	12.5	0.34	5.0
50.0	27.4	0.29	4.7	28.0	17.7	0.54	6.8
			Millstone Grit				
56.5	25.0	0.19	2.1	48.1	35.0	0.50	4.0
50.0	36.0	0.48	3.4	50.0	27.4	0.29	2.1
50.0	36.2	0.48	3.4	49.0	23.4	0.25	2.5
50.0	43.5	0.72	5.2	49.2	23.2	0.24	2.3
48.0	46.1	0.91	7.2	50.0	0.0	0.05	1.8
48.0	48.2	0.99	13.0	28.2	14.0	0.42	2.0
47.2	40.2	0.70	5.2	29.0	17.8	0.51	3.0
47.0	40.0	0.70	4.3				
			Kentish Rag				
50.5	46.2	0.80	10.2	56.5	25.0	0.19	4.2
50.0	33.8	0.43	7.2	50.0	36.0	0.48	6.8
50.0	34.0	0.43	7.3	50.0	36.0	0.48	6.8
54.0	28.0	0.27	5.7	50.0	43.5	0.72	6.0
56.0	31.0	0.27	5.9	50.0	46.0	0.82	11.0
51.0	19.0	0.17	4.0	48.0	46.1	0.91	11.0
51.0	19.0	0.17	3.7	24.0	0.0	0.21	5.1
53.0	0.0	0.04	1.5	26.2	14.0	0.50	7.2
53.0	0.0	0.04	2.0	21.0	16.0	0.73	9.0
53.0	20.2	0.17	4.2	20.8	18.7	0.88	12.0
			Chalk				
51.2	22.0	0.20	3.4	52.0	37.0	0.46	5.1
49.5	29.2	0.34	3.4	47.0	40.0	0.70	5.1
49.8	40.3	0.61	5.7	50.7	47.3	0.85	10.0
51.5	45.5	0.73	7.4	49.6	41.6	0.68	4.7
51.2	44.0	0.70	7.0	27.8	14.0	0.41	6.3
49.5	36.4	0.51	7.0	28.7	17.8	0.51	8.0
50.0	17.0	0.16	2.3				

TABLE I (continued)

Temperature Upper	Lower	Relative humidity	x/m × 1000	Temperature Upper	Lower	Relative humidity	x/m / 1000
			Portland Stone				
50.1	22.0	0.21	2.7	52	37.0	0.46	1.5
48.6	29.2	0.34	2.4	52	40.0	0.55	2.6
49.6	40.3	0.62	3.1	50	46.0	0.81	3.0
51.2	45.5	0.74	3.3	50	41.6	0.65	2.4
50.3	44.0	0.73	3.6	28.0	14.0	0.42	3.0
49.5	36.4	0.51	3.3	30.0	17.8	0.48	4.0
			Monk's Park Stone				
56.5	25.0	0.19	1.5	50.0	43.5	0.72	4.2
50.0	36.0	0.48	2.5	48.0	46.1	0.91	3.2
50.0	36.2	0.48	2.5	48.2	48.0	0.99	3.9
			Dolomitic Limestone (room temp.)				
23.5	0.0	0.21	1.0	21	18.1	0.83	3.3
23.3	10.0	0.63	2.1	14.5	13.0	0.90	4.3
			Buxton Limestone (room temp.)				
22	17.4	0.70	0.0	20.0	18.0	0.90	0.0
21	18.7	0.80	0.0				
			Stoneycombe Stone (room temp.)				
23.2	17.2	0.70	0.0	21.6	19.4	0.88	0.00
21	17.4	0.82	0.0				
			BRICKS				
			Red Rubber				
16.2	14.2	0.92	0.0	16.4	16.2	0.98	0.0
			Red Wire-Cut				
24.0	19.0	0.70	0.0	19.0	19.0	1.0	0.0
			Blue Wire-Cut				
20.0	20.0	1.0	0.8	18.0	18.0	1.0	1.4
			Blue Stafford				
20.0	20.0	1.0	0.5	15	15	1.0	1.0
20.5	18.7	0.85	0.0 (after standing four months).				
			Fletton Brick				
17.0	17.0	1.0	2.5	20.5	10.5	0.50	0.0
			Stock Brick				
50.0	17.0	0.16	0.0	50.8	41.6	0.62	1.2
52.0	37.0	0.46	1.0	50.0	49.0	0.95	1.6
47.0	40.0	0.70	1.0				
			Sand-Lime Brick (unheated during evacuation).				
50.0	17.0	0.16	3.0	50.0	46.0	0.81	5.2
52.0	37.0	0.46	3.0	50.0	49.0	0.96	8.0
49.0	41.6	0.68	4.7				

TABLE I (continued)

Temperature Upper	Temperature Lower	Relative humidity	x/m × 1000	Temperature Upper	Temperature Lower	Relative humidity	x/m × 1000
Sand-Lime Brick (heated during evacuation)							
56.5	25.0	0.19	11.2	47.2	40.2	0.70	14.2
50.0	36.2	0.48	14.7	47.0	40.0	0.70	14.0
50.0	36.2	0.48	14.7	48.1	35.0	0.50	11.9
52.5	43.5	0.64	14.9	50.0	27.4	0.29	12.7
50.0	43.5	0.72	14.9	49.0	23.4	0.25	12.0
48.0	46.1	0.91	15.1	49.2	43.2	0.24	12.7
48.2	48.0	0.99	16.6	50.0	0.0	0.05	11.0
GRANITE							
19.0	19.0	1.0	1.5	18.1	16.0	0.88	0.0
MISCELLANEOUS SILICEOUS MATERIALS							
Powdered Clear Quartz Crystal							
24.0	0.0	0.20	0.0	20.0	19.0	0.94	0.0
20.7	17.2	0.83	0.0				
Leighton Buzzard Sand							
50.0	26.0	0.27	0.5	24.0	0.0	0.20	1.0
50.0	33.8	0.43	1.6	21.0	16.0	0.70	1.5
50.0	34.0	0.43	2.4	20.7	17.2	0.83	3.0
50.5	46.2	0.80	2.0	17.2	16.1	0.90	3.0
Fibres of Fused Silica							
50.0	26.0	0.27	1.0	24.0	0	0.20	1.0
50.0	33.8	0.43	2.1	21	16	0.70	3.0
50.5	46.2	0.80	3.0	17.3	17	0.97	5.0
Kieselguhr							
50.5	46.2	0.80	60	50.0	36.2	0.48	30.0
50.0	33.8	0.43	58.0	52.5	43.5	0.64	41.0
50.0	34.0	0.43	58.0	50.0	43.5	0.72	51.0
54.0	28.0	0.28	30.5	48.0	46.1	0.91	55.3
56.0	31.0	0.27	27.3	48.0	40.2	0.99	65.0
51.0	19.0	0.17	22.0	47.2	40.2	0.70	58.0
51.0	19.0	0.17	23.3	47.0	40.0	0.70	57.0
54.0	20.0	0.16	22.5	48.1	35.0	0.50	52.6
53.0	0.0	0.04	14.7	50.0	27.4	0.29	32.0
53.0	0.0	0.04	15.0	49.0	23.4	0.25	29.0
53.0	20.2	0.17	16.0	49.2	23.2	0.24	29.0
56.5	25.0	0.19	16.0	49.0	0.0	0.05	16.7
50.0	36.0	0.48	29.0	50.0	−40	0.003	10.0

TABLE I (continued)

Temperature Upper	Temperature Lower	Relative humidity	x/m × 1000	Temperature Upper	Temperature Lower	Relative humidity	x/m × 1000
			Filter Cel				
50.5	46.2	0.80	87.7	50.0	43.5	0.72	70.1
50.0	33.8	0.43	72.9	48.0	46.1	0.91	80.0
50.0	34.0	0.43	74.3	48.2	48.0	0.99	82.1
54.0	28.0	0.28	41.6	47.2	40.2	0.70	72.0
56.0	31.0	0.27	39.3	47.0	40.0	0.70	72.4
51.0	19.0	0.17	29.5	48.1	35.0	0.50	67.3
54.0	20.0	0.16	30.9	50.0	27.4	0.29	44.8
53.0	0.0	0.04	20.8	49.0	23.4	0.25	38.3
53.0	20.2	0.17	23.0	49.2	23.2	0.24	38.0
56.5	25.0	0.19	25.9	49.0	0.0	0.05	23.5
50.0	36.0	0.48	40.0	50.0	22.0	0.21	27.2
50.0	36.2	0.48	41.0	49.2	28.8	0.34	32.7
52.5	43.5	0.64	64	49.7	40.3	0.62	44.7
				50.0	45.5	0.80	61 8
			Gatton Stone				
50.5	46.2	0.80	58.4	50.0	43.5	0.72	41.2
50.0	33.8	0.43	36.1	48.0	46.1	0.91	66.1
50.0	34.0	0.43	35.6	48.0	48.2	0.99	62.0
54.0	28.0	0.28	25.3	47.2	40.2	0.70	33.6
56.0	31.0	0.27	25.5	47.0	40.2	0.70	37.9
51.0	19.0	0.17	20.7	48.1	35.0	0.50	26.4
51.0	19.0	0.17	20.9	50.0	27.4	0.29	20.0
54.0	20.0	0.16	21.1	49.0	23.4	0.25	17.1
53.0	0.0	0.04	13.7	49.2	23.2	0.24	17.0
53.0	0.0	0.04	14.0	49.0	0.0	0.05	11.1
56.5	25.0	0.19	20.0	50.0	22.0	0.21	17.1
50.0	36.0	0.48	27.0	48.6	29.2	0.34	19.5
50.0	36.2	0.48	28.0	49.6	40.3	0.62	29.1
52.5	43.5	0.64	38 0	50.7	45.5	0.76	43.0
			Filter Cel (specially evacuated)				
49.3	−39.0	0.01	4.8	50.2	36.5	0.49	37.4
49.5	−20.0	0.03	4.4	48.5	43.9	0.79	54.6
49.8	−20.9	0.03	4.3	48.2	43.9	0.80	55.0
49.0	0.0	0.05	8.1	50.8	37.8	0.51	52.1
50.0	6.1	0.08	12.0	49.6	32.5	0.41	45.9
50.4	6.5	0.08	12.0	50.2	32.5	0.40	46.9
50.0	8.2	0.09	13.9	49.0	28.5	0.33	40.6
50.8	9.0	0.09	14.4	50.0	28.5	0.31	39.2
51.0	16.5	0.14	16.2	48.2	14.5	0.15	25.8
48.5	16.0	0.16	17.0	49.0	15.0	0.15	26.5
49.7	25.3	0.26	22.8	48.2	0.0	0.06	13.4
49.0	25.2	0.27	24.0	49.0	1.4	0.06	14.2
50.8	30.3	0.33	29.2	50.5	−31	0.03	9.5
49.9	30.3	0.34	30.5	51.0	−28	0.03	8.1
49.7	36.5	0.50	37.9				

TABLE I (Continued)

Temperature Upper	Lower	Relative humidity	x/m × 1000	Temperature Upper	Lower	Relative humidity	x/m / 1000
Millstone Grit (Darley Dale).				Stancliffe Stone. (2nd. tube)			
17.2	−11.0	0.13	1.7	50.5	25.3	0.25	1.7
17.2	− 6.9	0.18	2.2	51.2	25.2	0.24	1.7
17.2	2.4	0.37	3.7	51.2	30.3	0.32	2.4
17.2	2.4	0.37	3.5	50.4	30.3	0.34	2.5
17.9	9.8	0.56	4.0	50.8	36.5	0.49	3.7
17.9	9.9	0.56	4.0	50.3	36.5	0.50	3.5
18.0	15.0	0.82	5.5	49.0	43.9	0.78	5.7
17.8	14.8	0.82	6.0	49.5	43.9	0.77	6.3
17.4	14.4	0.82	6.0				
Dolomitic Limestone. (2nd. tube)							
17.0	−20.0	0.06	0.0	49.5	18.5	0.18	0.0
17.0	−10.0	0.14	0.3	50.6	30.2	0.33	1.0
16.0	− 4.5	0.20	0.6	50.0	37.1	0.52	2.1
15.2	3.2	0.45	1.3	50.3	44.0	0.72	3.4
15.0	7.9	0.63	2.3	49.7	47.2	0.89	4.1
15.4	13.1	0.86	3.6				
Chalk (2nd. tube)							
18.0	2.9	0.35	2.9	51.2	25.2	0.24	1.7
17.9	2.9	0.35	2.9	51.2	30.3	0.32	2.0
17.2	11.0	0.67	6.0	50.4	30.3	0.34	2.2
17.2	14.0	0.81	6.0	50.8	36.5	0.49	4.0
17.2	14.0	0.81	6.0	50.5	36.5	0.50	3.8
17.9	16.0	0.88	9.1	49.0	43.9	0.78	7.0
17.9	16.0	0.88	9.1	49.5	43.9	0.77	7.2
50.5	25.3	0.25	1.4				

Discussion of Results obtained with Water Vapour

The results given in the preceeding tables are shown in graphical form. Figs. 2-4 embrace all the materials giving any sorption at all which did not show hysteresis.

Consideration of the graphs and the tables shows that the materials studied may be divided into three groups: (1) those which sorb practically no water at all or, where the small amount taken up remains constant over a wide humidity range; (2) those which sorb a small quantity, 1% or less, which varies somewhat with changing humidity; and (3) those which sorb a large amount of water (of the order of 10%) at high humidity and in which the amount sorbed varies greatly with the humidity conditions.

The first group includes pure quartz, pure limestones, and the bricks which have been burned or fired at a high temperature and also the granite studied. These materials take up practically nothing from saturated water vapour. All these materials are practically immune to humidity changes.

Moreover we can include in this group Portland stone and Monk's Park stone. These show no variation of the amount of water sorbed, over a wide

range of humidity, though a small amount of water is taken up on exposing them to water vapour. This is probably due to chemical combination with lime etc. In any case, the really important point is not the absolute amount of water sorbed, but the rate of variation of this amount with the humidity, as shown by the gradients of the curves expressing this relationship.

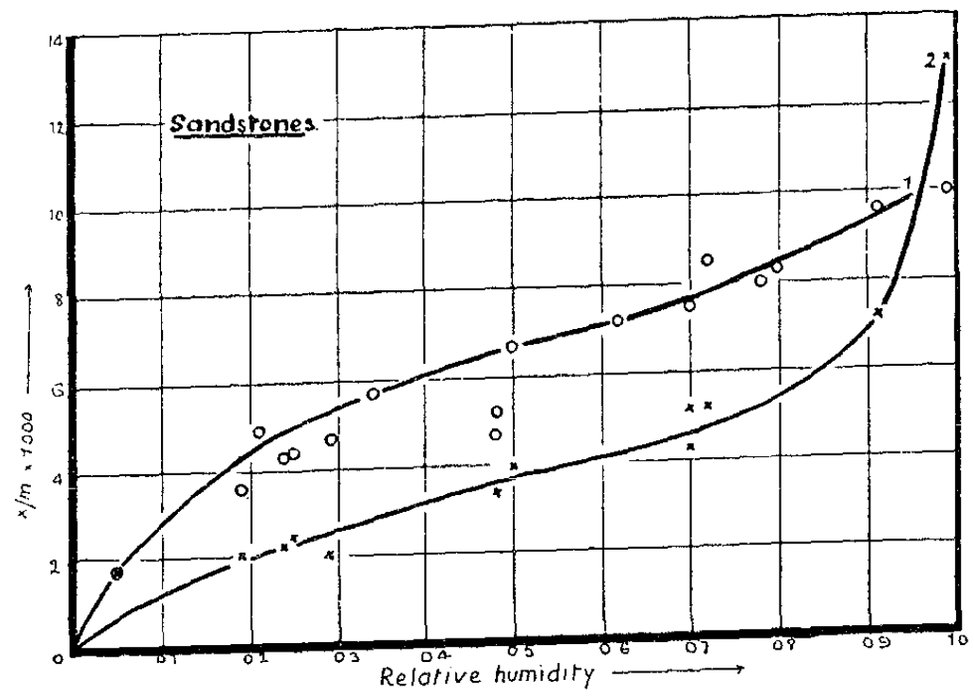


FIG. 2
1. Sandstone 50°C.
2. Millstone Grit 50°C.

Most of the bricks take up practically no water in an almost saturated atmosphere but we know from experience that when any of these bricks are immersed in water a relatively large amount of water is imbibed (red rubber 13%, Fletton 6-9%, Stock bricks 20%). The discrepancy is explained by the fact that the absorption from liquid water is not a case of adsorption by a colloid, but merely the filling up of the large or macroscopic pores in the brick. The water-immersion absorption figures merely measure the porosity of the material. The figures given in the table however give the amount of water taken into the colloidal constituents. *They are therefore measures of the amounts of colloid in the materials.* Bricks show no sorption and therefore have no colloidal constituents in this sense.

The second group includes ordinary building stone, such as the better sandstones which show only a small sorption. However, when this sorption is referred to the actual amounts of colloid material it becomes quite considerable. Thus the Idle Quarry sandstone examined sorbed only 1% of its total weight (at approximately saturation). It however consists of 88% of SiO_2 plus 12% CaO, MgO, Fe_2O_3. Most of the silica is present as quartz crystals, the remainder being combined with the metallic oxides to form binding material. If we assess this colloidal binding material as 10% of the weight of the stone, we see that this binding material, which alone is reactive,

sorbs 10% of its weight in a saturated atmosphere—and is therefore quite comparable with the substances in group 3. The artificial sand-lime brick must also be included in the second group.

The materials in the third group consist largely of amorphous silica as for example Kieselguhr, Filter Cel, Gatton stone. It is important to remember

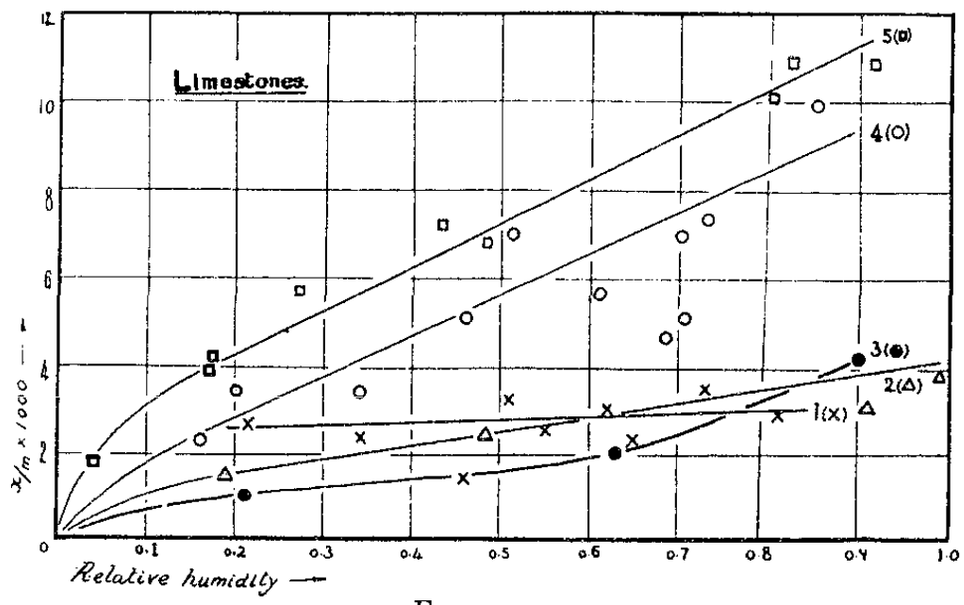


FIG. 3

1. Portland Stone at 50°C.
2. Monk's Park Stone at 50°C.
3. Dolomite Limestone at 20°C.
4. Chalk at 50°C.
5. Kentish Rag at 50°C.

that in contrast to these the crystalline silica, quartz, sorbs practically no water even in an almost saturated atmosphere; for it proves that the sorption exhibited by sandstone, and hence all the trouble due to swelling, is due to the amorphous binding material in the sandstone.

Microscopic examination of sandstones indicates that they are composed of small grains of quartz embedded in an amorphous cementing material, which in some cases may consist of calcium or magnesium silicates and in others may be calcium or magnesium carbonates.

This cementing substance resembles a gel. For example, as will be shown, it can be stained with dyes, and it sorbs water vapour in amounts varying continuously with the vapour pressure. On imbibing water, the sandstone increases distinctly in volume, paralleling the behaviour of organic gels.

In ordinary building stones, what colloidal gels exist, are present in small amount. But in the case of calcareous hydraulic cements such as Portland cement, it is now generally believed that the set cement consists mainly of gels of calcium silicate, and perhaps of calcium aluminate, hardened by desiccation. This view was first advanced by Michaelis[1] and has received considerable support, especially as a result of the researches of the U. S. Bureau of Standards.[2]

[1] Chem. Ztg., **17**, 892 (1893).
[2] A. A. Klein and A. J. Phillips: U. S. Bur. Standards, Technological Paper **43** (1914); P. H. Bates and A. A. Klein: **78** (1916).

Even in the case of an ordinary lime mortar, and in plaster of Paris, it seems that the tenacity of the material is due to the presence of a gel.

Desiccated colloidal substances such as glue possess high tensile strength which we should ascribe to linking of the micelles by dehydration. That a structure with irregularly oriented units such as we assume an amorphous

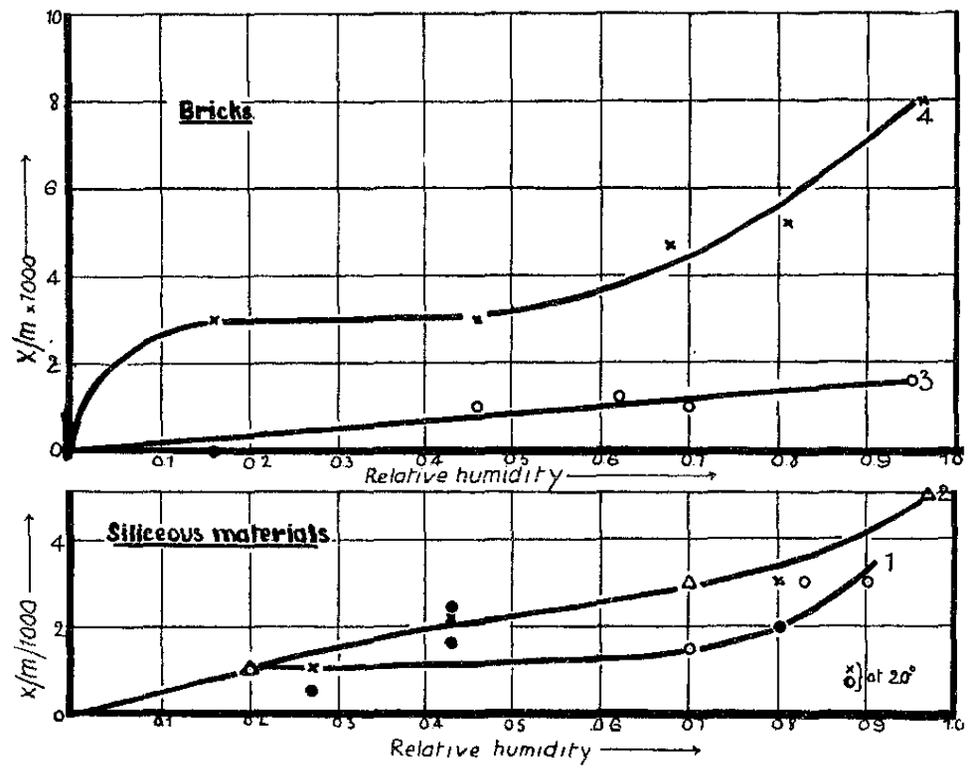


FIG. 4

1. Leighton Buzzard Sand
2. Fibres of Silica
3. Stock Brick
4. Sand-lime Brick (unheated) at 50°C

substance to be, should possess a high tensile strength compared with a crystal, is easily understood when we consider the existence of cleavage planes, glide planes etc. in the latter.[1]

As all gels shrink on drying and expand on absorption of water, considerable movements may result in cement from this cause. Moreover, the hydration processes with production of gel continue slowly in the interior of a cement long after the mass has set. In addition slow dehydration of the gels already present goes on. Thus a series of complicated volume changes occur causing internal stresses.

Any method for the prevention of this slow periodical hydration and dehydration in the case of certain stones and cement must be based primarily on an intimate knowledge of the colloidal structure of the materials used.

From the results with pure limestones it may be suggested that the cohering of such limestones is not due to the presence of an inter-grain colloidal cement, and probably not to the interlocking of crystals of calcium carbonate, but rather to their true adhesion according to the hypothesis of McBain and Lee.

[1] McBain and Lee: Proc. Roy. Soc., **113**, A, 606 (1927).

Hysteresis observed with Kieselguhr, Filter Cel and Gatton Stone

Figure 5 illustrates for Gatton stone the hysteresis that was observed with three materials; namely, Gatton stone, Filter Cel and Kieselguhr, all containing large amounts of colloidal silica. The phenomenon is well known from the classical studies of van Bemmelen on silicic acid allowed to set without stirring. Apart from the obvious proof of the existence of colloidal materials

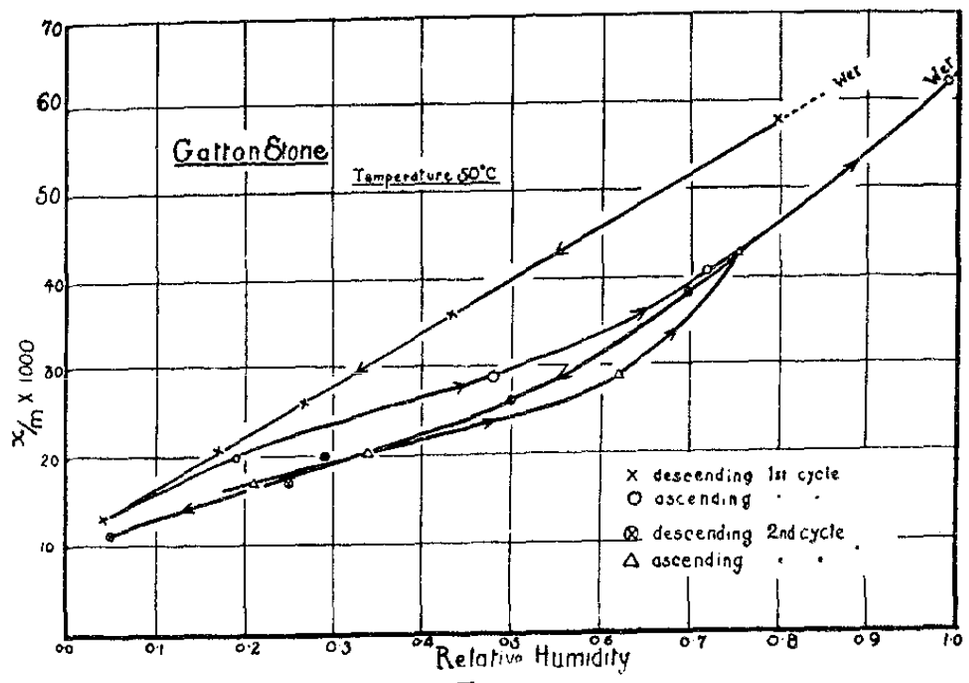


FIG. 5

in this type of (unsatisfactory) building material, the data are of great interest in showing the permanent change that is occasioned in such stone by its first dehydration after removing from a wet quarry. A process that is only completed by subsequent cycles of humidity change, such as are illustrated in the single recorded experiment.

Zsigmondy was the first to explain such curves on the basis of the micellar theory on the assumption that the material is a loose aggregate of ultramicroscopic colloidal particles or micelles. The surface of each micelle is shown to be capable of true adsorption, perhaps only one molecule deep, but the relatively large caverns and interstices so coated form pores playing the role of capillary tubes in which liquids may condense in bulk. According to our extension of the micellar theory the colloidal particles are linked together at the points of contact and this coupling may be effected by dehydration.

There are two current explanations of the hysteresis observed when emptying and filling the pores respectively. In the first explanation the emptying is assumed to be due to evaporation from the curved liquid surface, whereas when filling the wetting is less complete, the contact angle if any is greater and therefore the vapour pressure for a given amount is higher. According to this suggestion the hysteresis should be largely confined to the steepest portions of the curve (for Kieselguhr and Filter Cel between the

relative humidities of 0.27 and 0.4); whereas, in all our cases hysteresis is observable throughout. According to the second explanation the hysteresis is ascribed to air entering the emptied pores and interfering with their wetting and filling, and Patrick has shown that thorough evacuation can largely eliminate such hysteresis.

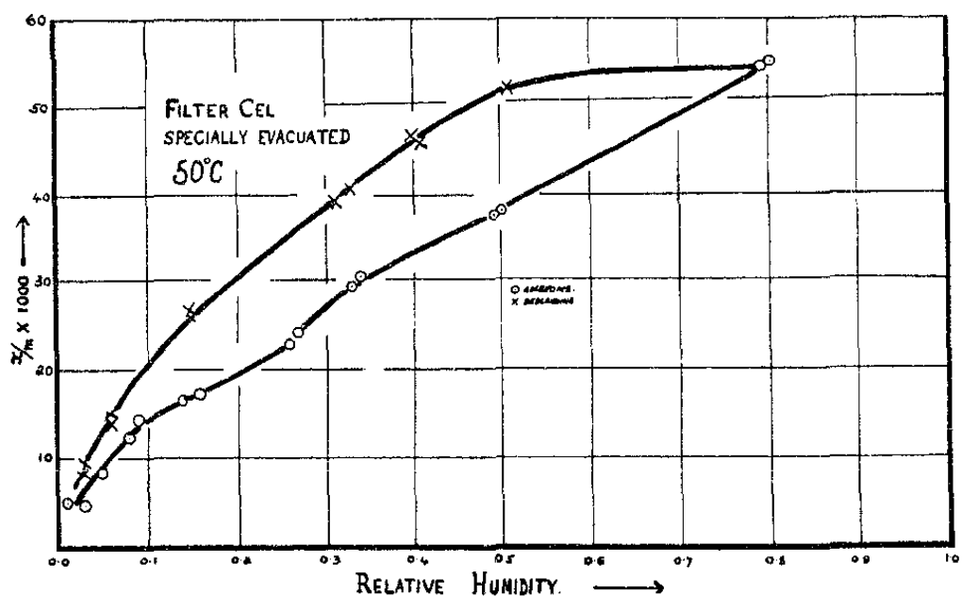


FIG. 6

This however is not the case with the materials here studied. A sample of Filter Cel was specially prepared for measurement by employing a vacuum of 0.00001 mm. and four times in succession pure water vapour was introduced, allowed to condense upon the Filter Cel and again completely removed by evacuation at 200°C. Thereupon the experiments recorded in the table were carried out with the results shown in Fig. 6 where hysteresis is still observed. The curves are however no longer of the form familiar through the work of van Bemmelen and his successors such as Zsigmondy, Anderson and Patrick. We therefore seek a third explanation of this portion or type of the hysteresis and we find it in the micellar theory already mentioned.[1]

The actual swelling of these "rigid" gels has been measured at the Building Research Station and it has even been shown there by F. T. Meehan that charcoal in adsorbing a gas such as carbon dioxide likewise swells appreciably. This we would attribute to an uncoupling of certain linked particles through double decomposition; that is, through addition of a molecule of water to each valency bond thus broken and exposed. Incidentally, this uncoupling through satisfaction of the valencies with mutually independent molecules of water should not only loosen but weaken the structure. On the whole, much of the coupling should tend to be irreversible, the stone should shrink and become stronger and less susceptible to moisture change. For example, sorption of nitrocotton may be reduced to two thirds of its original value by this means.

[1] See, for example, McBain: J. Phys. Chem., **30**, 239 (1926).

Finally, for interest it may be noted that the largest pores in Filter Cel and Kieselguhr are about 9 Ångstrom units in diameter and that condensation of water at relative humidities of 0.3 and 0.4 would take place in capillaries of 7.7 and 10.1 ångstrom units in diameter respectively.

Sorption of Dyes by Building Materials

The staining of minerals by dyes has been used as a criterion of their colloidal nature.[1] This method has limitations. A few crystalline minerals, owing to their enormous basal surfaces notably, mica and kaolinite, also take up dyestuffs. Moreover the amount of dye adsorbed depends on the degree of dispersion of the material. Dyes are also used for estimating the colloid content of soils.[2]

It is interesting to find that a parallelism exists between the sorptive capacity of the building materials for water, and their absorption of dyes. For this purpose two dyes were employed; viz. methylene blue, and magenta. Dilute solutions of methylene blue, mixed with dilute solutions of either hydrochloric acid, caustic soda, or calcium hydroxide, underwent no change in shade, compared with a blank consisting of dye solution mixed with distilled water, and made up to the same value as the acid and alkali mixtures. The magenta solutions on the other hand were precipitated by lime water, the colour base separating. Hence, before treatment with the magenta solution, lime had to be removed from the building stones by means of ammonium oxalate.

In the case of methylene blue, quantities of one gram of fairly well powdered samples of the stones, were each shaken thoroughly in stoppered test tubes with 10 cc of an aqueous solution of 1 gram of methylene blue in 5 litres, and then allowed to settle, when the shade of the supernatant liquid was observable. With magenta, the samples were first treated with 15 cc. of saturated ammonium oxalate solution, and well shaken.

After standing 24 hours, the tubes were centrifuged, and the supernatant solution poured off. Distilled water was then added and centrifuging repeated. This was done six times. After being thus washed free from ammonium oxalate, 10 cc of the magenta solution (1 gram dye per 5 litres of distilled water) were added, and the tubes shaken up and allowed to settle.

From Table II it is seen that the order of increasing dye stuff absorption is practically the same for each dye.

The order of colloidality as determined by the staining methods is apparently in agreement with that deduced from sorption experiments with water vapour. Thus the bricks and quartz take up practically no dye, in agreement with the sorption experiments indicating their non-colloidal nature. The non-colloidal nature of the limestone is also well shown by the zero or negligible dye absorption, while the definitely colloidal sandstones react markedly.

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[1] Dittler: Kolloid-Z., **4**, 277; **5**, 93; Endell: 244 (1909).
[2] U. S. Dept. Agriculture, Prof. Paper, Bull. 1193 (1924).

The only notable disagreement between the two methods is shown by granite. This is probably due to the presence of the mica in the granite, since, as already mentioned, mica adsorbs dye.

TABLE II

Methylene blue		Magenta	
Substance	Shade of supernatant liquid	Substance	Shade of supernatant liquid
1. Red wire-cut brick.		1. Red wire-cut brick.	
2. Red rubber brick.		2. Stock brick	Indistinguishable from blank.
3. Stock brick.	Indistinguishable from blank.	3. Red rubber brick.	
4. Quartz powder.		4. Stoneycombe stone.	Very slight lightening of shade in direction 3 to 7.
5. Stoneycombe stone.		5. Buxton limestone.	
6. Buxton limestone.		6. Dolomitic limestone.	
7. Dolomitic limestone.	Exceedingly slight lightening of shade.	7. Portland stone.	Almost indistinguishable from blank
8. Portland stone.	Rather lighter than above.	8. Granite.	Slight lightening in shade.
9. Granite.	Considerably lighter than blank.	9. Sand-lime brick.	
10. Kentish Rag.	Liquid only tinged colour. Depth of shade decreasing from 10 to 12.	10. Chalk.	
11. Sand-lime brick.		11. Kentish Rag.	
12. Chalk		12. Millstone	Colour almost completely abstracted.
13. Millstone grit.	Colour completely removed.	13. Sandstone.	
14. Sandstone.		14. Gatton stone.	Absolutely colourless.
15. Gatton stone.			

The order of decreasing intensity of shade was observed within an hour of adding the dye-stuff. On keeping the solutions in contact with the materials, it was observed that the order and colour intensity remained unchanged, even after three months, in the case of methylene blue. The magenta solutions faded however in some cases after 24 hours. This applied to the carbonates (Portland stone, Stoneycombe stone, Buxton and Dolomitic limestones). This fading was probably due to the formation of free lime in solution. Hence methylene blue is a much more satisfactory reagent than magenta for this purpose.

Effect of Heat on Colloidal Structure

The application of colloid chemistry to mineralogy and petrology is a development of the present century. Such studies originated with Cornu[1] and his co-workers, but little has been done except in developing methods for the recognition and classification of colloid minerals. The literature is very scattered, but two extensive summaries have appeared, one by Marc and Himmelbauer[2] and the second by Scott.[3]

The non-colloidal character of burned bricks has already been noted. This is a significant observation. They are prepared from a colloidal substance—clay—and hence it must be concluded that the high temperature to which they are subjected during manufacture effectively destroys the colloid present. This is in accord with the observation of Bouyoucos[4] that soils (and also silica gel) on heating to 800°C, lose their colloid character, as manifested by dye sorption, heat of wetting, and plasticity.

To confirm this, samples of powdered sandstone placed in a platinum capsule were heated in a silica tube in a small oven for three hours to temperatures of 500°C. 680°C and 800°C respectively. Small quantities of the heated samples were then employed in water sorption experiments. The results were as follows:

	Relative humidity	x/m × 1000
1. Sandstone heated to 900°	0.89	0.0
2. Sandstone heated to 680°	0.60	1.0
	0.73	2.0
	0.99	6.0
3. Sandstone heated to 500°	0.54	6.1
	0.99	11.0

Thus after being heated to 900° sandstone sorbs no water vapour even in an almost saturated atmosphere, showing that the colloidal structure has been completely destroyed by heating.

After heating to 680° the power of sorbing water has been diminished, but heating to 500° apparently does not alter the colloidal structure markedly, since the sorption exhibited at the humidities given is comparable with that of untreated stone.

The absorption of methylene blue by sandstone and Gatton stone heated to several different temperatures was also determined:

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[1] F. Cornu: Kolloid-Z., **4**, 15 (1909).
[2] R. Marc and A. Himmelbauer: Fortschritte Min. Kryst. Petr., **3**, 33 (1913).
[3] A. Scott: "Fourth Report on Colloid Chemistry," 204 (1922), now under revision.
[4] Bouyoucos: Soil Science, **17**, 135 (1924).

Temperature	Sandstone Colour of dye solution
960°C	Indistinguishable from blank.
940	Very slight lightening in shade.
850	Solution colourless.
750	Solution colourless.
	Gatton Stone
950	Indistinguishable from blank.
850	Slight lightening in shade.
750	Solution colourless.

Again as shown by dye absorption, the effect of heating to 900°C is to destroy the colloidal matter present. The suspension settled slowly until the material had been heated to 900°C.

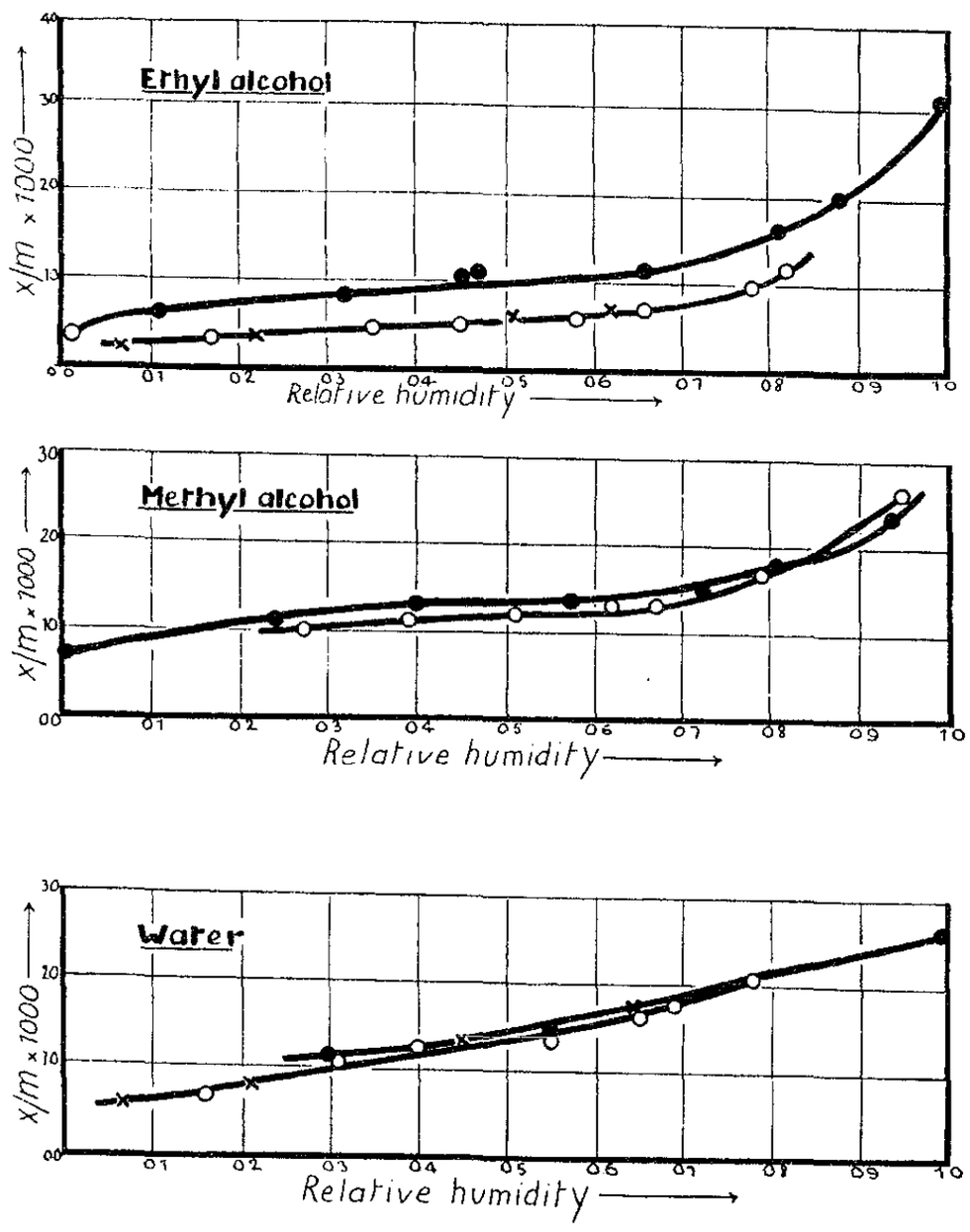


FIG. 7

● 18°C. ○ ascending 50°C × descending 50°C

Sorption of Various Liquids by the Intergrain Cement present in Sandstone

Colloids are characterised by dehydration curves free from any sharp discontinuity but this characteristic is shared by the incompletely studied group of minerals related to the zeolites. A good deal should be deducible from the study of the exact shape of these sorption curves, and the type to which they belong.

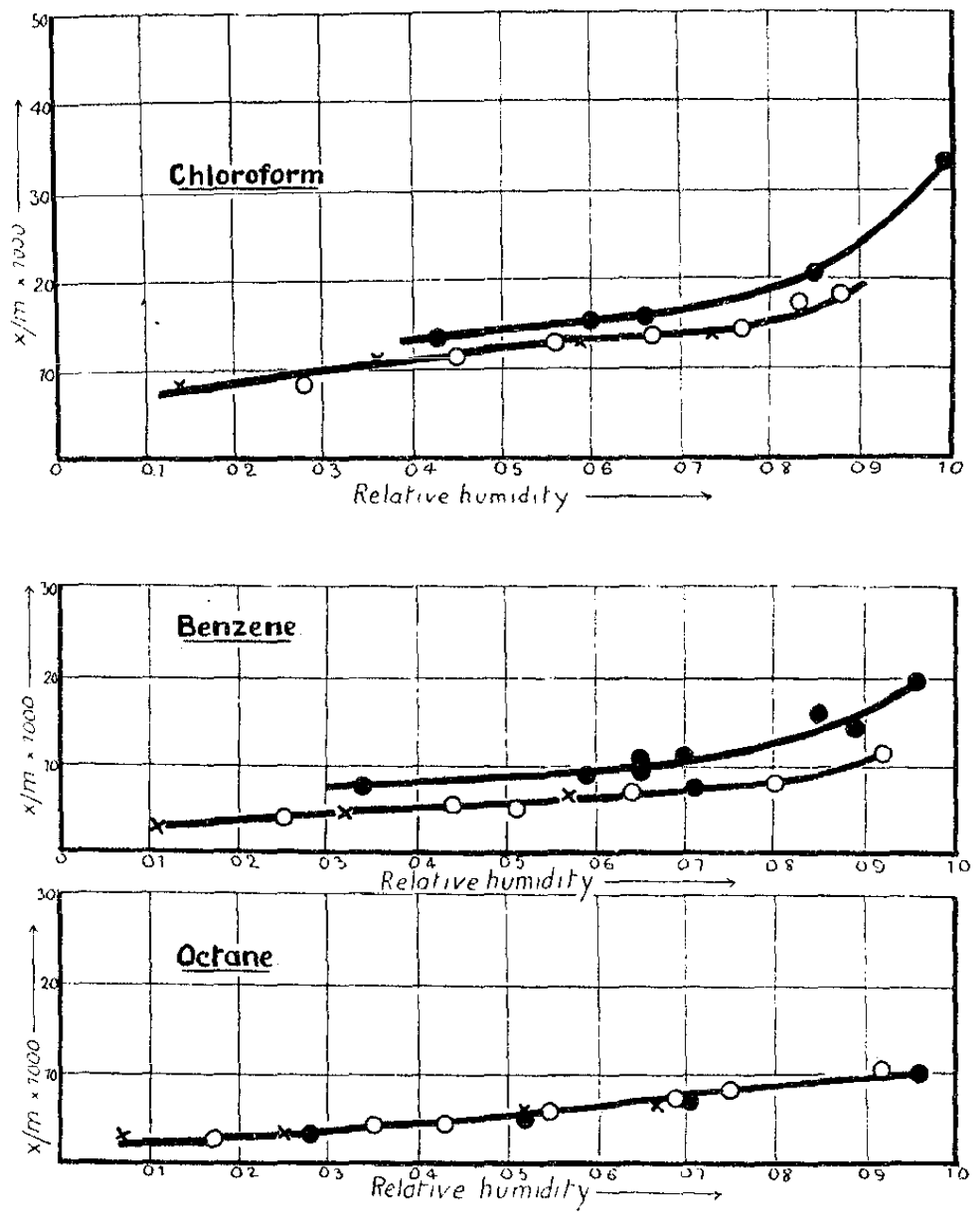


FIG. 8

● 18°C. ○ ascending 50°C × descending 50°C.

Weigel[1] has shown that the zeolite chabasite absorbs large amounts of the vapours of ethyl and methyl alcohols and formic acid, but takes up practically no acetone, ether, or benzene. McBain[2] has pointed out that this can be

[1] Z. Krist., **61**, 135 (1924).
[2] Kolloid-Z., **40**, 1 (1926).

explained on the assumption that the interstices in the zeolite crystal lattice are too small to admit the larger molecules of the latter liquids, and on this basis has calculated the size of the openings to be less than five Ångstrom units. This therefore presents one distinctive type.

The active material or cement in the sandstone might conceivably consist of hydrated crystals of the zeolite type, or it might be a gel consisting of an agglomeration of ultramicroscopic crystals, or a gel in which the units are noncrystalline, or lastly, a glass. This should be determinable if the active material could be isolated and its sorption carefully studied with various liquids. Determination of the nature and structure of this cement should lead to methods for the destruction or the inactivation of the cement, preferably without destroying its cementing properties. Preliminary measurements of sorption have been carried out with two samples in which the colloidal material in sandstone has been concentrated by elutriation.

For this purpose, some pieces of sandstone were ground somewhat finely in an agate mortar, and the powder placed in a flask containing distilled water, which was then shaken violently. The mixture was then allowed to settle for half a minute (which was quite sufficient for the fairly larger compact grains of quartz to settle out), and the supernatant liquid poured off and filtered. The contents of the filter paper were then dried in the steam bath. The specimens thus obtained were of a pronounced yellow shade.

Results of the sorption experiments are presented in Tables III and IV and in Figs. 7 and 8. It should be pointed out at once that the elutriation has effected at least a partial concentration of the colloidal matter since the sorption is about doubled. Further, the curves, particularly with specimen 1, exhibit a distinct S-shape similar to that of certain gels.

TABLE III

Sorption by Inter-grain Cement of Sandstone. (Sample 1)

Temperature Upper	Temperature Lower	Humidity %	x/m × 1000	Temperature Upper	Temperature Lower	Humidity %	x/m × 1000
			Water				
18.0°	15.0°	0.83	26.0	52.0	22.0	0.19	9.4
18.0	0.0	0.30	14.6	50.0	29.6	0.34	12.0
18.0	9.1	0.56	17.4	50	34.1	0.43	13.7
19.1	15.7	0.78	24.1	51	38.7	0.52	16.4
18.2	18.1	0.99	36.7	50.0	42.7	0.68	18.6
16.7	14.0	0.84	29.5	49.3	44.1	0.77	22.3
16.0	12.5	0.79	26.9	50.3	46.8	0.84	27.2
16.6	11.1	0.69	20.6	50.2	41.7	0.64	18.0
17.1	8.5	0.55	17.2	50.4	36.7	0.53	15.0
17.1	3.8	0.30	14.3	52.0	23.0	0.21	7.7
				50.5	3.0	0.07	4.9
			Chloroform				
51.0	22.0	0.31	13.8	49.3	44.1	0.82	22.8
50.0	29.6	0.45	15.5	51.0	46.8	0.85	23.3
49.0	34.1	0.58	17.2	49.8	41.7	0.75	20.0
50.0	38.6	0.68	15.7	50.3	36.7	0.61	16.5
52.0	42.7	0.73	19.4	50.5	3.0	0.14	12.1

TABLE IV

Sorption by Inter-grain Cement of Sandstone. (Sample 2.)

Temperature Upper	Temperature Lower	Humidity %	x/m × 1000	Temperature Upper	Temperature Lower	Humidity %	x/m × 1000
			Water				
17.6	14.2	0.80	19.7	50.0	38.7	0.55	13.0
17.8	8.6	0.55	14.0	51.0	42.7	0.65	15.7
17.8	0.0	0.30	11.0	51.4	44.1	0.69	17.3
18.0	8.0	0.55	14.0	51.6	46.8	0.78	20.0
18.0	18.0	1.0	24.4	50.3	41.7	0.64	17.3
52.0	18.2	0.16	6.4	52.0	36.6	0.45	13.1
51.4	29.6	0.31	10.3	52.0	23.0	0.21	8.0
51.2	34.1	0.40	12.1	50.0	3.0	0.07	5.5
			Ethyl alcohol				
18.0	−55	0.002	2.7	51.5	18.2	0.17	3.0
17.0	−40	0.01	3.2	51.0	29.6	0.35	4.1
17.5	−14.0	0.11	6.0	50.0	34.1	0.45	4.5
17.5	0.0	0.32	8.0	50.0	38.7	0.58	5.5
18.4	5.7	0.45	10.0	50.8	42.7	0.66	6.6
18.4	11.7	0.66	10.9	49.5	44.1	0.78	9.3
13.6	11.6	0.88	19.5	51.0	46.8	0.82	11.4
18.0	18.0	0.99	30.9	51.2	41.7	0.62	6.6
18.0	14.6	0.81	15.6	50.0	36.6	0.51	6.0
20.5	8.5	0.47	10.7	52.0	23.0	0.22	3.0
				49.6	3.0	0.07	2.5
			Methyl alcohol				
24.0	−35	0.02	7.0	50.0	22.0	0.27	10.0
19.0	− 4	0.24	10.8	50.1	30.1	0.39	10.8
19.0	4.0	0.40	12.7	51.0	36.3	0.51	11.6
18.0	8.9	0.57	13.1	50.0	39.5	0.62	12.8
20.0	15.1	0.73	14.7	49.2	41.2	0.67	13.0
18.5	15.0	0.81	16.4	50.0	45.0	0.79	16.2
15.8	14.8	0.94	22.8	49.0	48.1	0.95	26.0
18.0	18.0	1.0	66.0				
			Chloroform				
18.0	14.5	0.85	20.4	51.2	18.2	0.27	8.3
17.3	10.6	0.72	17.4	49.4	29.6	0.45	11.2
18.4	9.8	0.66	15.4	50.3	34.1	0.56	12.7
17.4	6.5	0.60	15.0	50.4	38.7	0.67	13.0
21.0	4.0	0.46	9.3	50.3	42.7	0.77	14.1
16.8	13.6	0.85	20.0	49.5	44.1	0.83	17.5
17.0	17.0	0.99	33.2	50.5	46.8	0.88	17.7
18.2	0.2	0.43	13.0	50.3	41.7	0.74	13.7
				51.5	36.6	0.59	13.0
				49.3	23.0	0.36	11.6
				49.8	3.0	0.14	8.3

TABLE IV (continued)

Temperature Upper	Lower	Humidity %	x/m×1000	Temperature Upper	Lower	Humidity %	x/m×100
				Benzene			
17.6	14.1	0.85	15.8	49.7	18.2	0.25	3.7
18.4	9.7	0.65	10.8	49.4	29.6	0.44	5.5
17.3	10.1	0.70	11.0	50.8	34.1	0.51	5.0
17.4	6.6	0.59	8.8	49.5	38.7	0.64	7.0
21.0	0.3	0.34	7.5	51.2	42.7	0.71	7.3
16.8	7.0	0.65	9.3	49.0	48.1	0.80	8.3
17.0	14.5	0.89	14.0	48.8	46.8	0.92	11.5
17.0	17.0	0.96	19.5	50.3	41.7	0.72	7.3
				49.2	36.6	0.57	7.5
				49.9	23.0	0.32	4.5
				49.8	3.0	0.11	3.0
				Octane			
18.8	9.0	0.52	4.4	52.0	18.2	0.17	2.3
19.0	8.5	0.51	3.8	51.0	29.6	0.35	4.1
20.0	0.0	0.28	3.0	52.0	34.1	0.43	4.3
17.5	12.2	0.70	7.1	51.2	38.7	0.56	5.8
19.0	12.5	0.64	5.6	50.7	42.7	0.69	7.3
19.1	19.0	0.96	10.0	51.0	44.1	0.75	8.5
				48.8	46.8	0.92	10.8
				51.1	41.7	0.67	6.4
				50.0	36.6	0.53	5.0
				50.0	23.0	0.25	2.9
				50.0	3	0.07	2.7

The amounts of various liquids taken up by the second specimen of intergrain cement are tabulated for comparison for two values of relative humidity, 0.3 and 0.8, in Table V.

TABLE V

Liquid	Humidity	Amount (× 100) taken up by 1 gm. Vol.	Weight	Humidity	Amount (× 100) taken up by 1 gm. Vol.	Weight
Water	0.8	2.0	2.1	0.3	1.0	1.0
Benzene		0.95	0.85		0.6	0.7
Methyl Alcohol		1.9	1.6		1.2	1.0
Ethyl alcohol		1.26	1.0		0.5	0.4
Chloroform		1.0	1.5		0.75	1.1
C_8H_{18}		1.2	0.8		0.45	0.35

It is seen that though there are variations from liquid to liquid all the substances are sorbed independently of whether the molecules are large or small. Certainly the substances with large molecules (benzene, octane) are not sorbed in such large amounts by weight as those with small molecules (water, methyl alcohol) but there is no complete blotting out as in the case of chabasite. The evidence points towards a gel or micellar structure rather than a skeleton space lattice such as is exhibited by dehydrated zeolites or certain catalytic

oxides or probably certain carbons. This is not surprising, because of the sedimentary origin of standstone. Water and chloroform are sorbed most and each to about the same extent. Possibly if accurate readings could be taken at humidities close to saturation the weights of the several liquids taken up would be more nearly in ratio of their densities. When sandstone is immersed in any one of these liquids, the weight taken up is proportional to the density of the liquid.

Heats of Sorption by Building Material

The heats of sorption are calculable by means of the Clapeyron-Clausius equation wherever we have values for the pressure corresponding to the same amount of sorption at any two temperatures. When the isotherms at various temperatures plotted against relative humidities are independent of the temperature, the heat of sorption is equal to the heat of condensation of the pure liquid. When the heat of sorption is greater the values for x/m are less at higher temperatures. The differential heats of sorption at temperatures between room temperature and 50° C. have been calculated for typical values of relative humidity, and the results are collected in Tables VI and VII, for building materials and Specimen II of intergranular cement of sandstone respectively. The heats involved are only a little greater than the heats of condensation of the vapour to pure liquid, given in the table for comparison. The heats are greater at low humidities.

TABLE VI

Heat of Sorption in Kg. Calories per gm. mol. of water vapour at 34°C*

Stone	Molecular Heat of Sorption at Humidities:		
	0.2-.04	0.5-0.7	0.8-0.9
"Sandstone"[1]	12.0	11.0	10.4
Millstone Grit	12.8	11.0	10.4
Chalk	12.5	10.4	10.4
Kentish Rag	10.4	10.4	10.4
Dolomitic limestone	——	——	10.4

TABLE VII

Heats of Sorption of Organic Liquids in kilogram calories per mol of liquid at 34°C

Liquid	Molecular Heat of Sorption at Humidities:			
	0.2-0.4	0.5-0.7	0.8-0.9	Pure liquid
Water	12.0	11.0	10.4	10.4
Methyl alcohol	12.0	10.4	9.1	9.1
Ethyl alcohol	19.6	12.6	11.0	10.2
Chloroform	——	9.9	8.7	7.7
Benzene	——	12.7	9.6	8.1
Octane	9.8	9.8	9.8	9.8

*Molecular heat of condensation of water = 10.4.

[1] From Table VII.

Stone Preservatives

Many substances and materials have been proposed as stone preservatives but it would seem clear that different types of stone would require different types of preservative and that different types of preservative are necessary to counteract different attacking and disrupting agencies. Pure limestone for example needs no preservative against fluctuation of humidity but rather against chemical attack.

Confining ourselves to the discussion of a preservative against effect of changes in humidity of materials such as sandstone, we proceed from the conception at which we have arrived for the mechanism of the swelling process. In the original structure the micelles of the intergranular gel are stuck to each other by residual valencies. When water vapour is sorbed its molecules have a superior attraction for the micelle valencies. They disrupt some of the valency bonds and appropriate the broken bonds. The action is the same as the loosening of a glass stopper by the penetration of an oil film which separates the two glass surfaces by uniting with each of them (McBain: loc cit).

It follows that if the free and disruptible valencies in the gel can be satisfied permanently with some substance, swelling is eliminated. To prevent the swelling, all that is necessary is to satisfy the valencies of the micelles permanently with a substance of higher chemical affinity for them than water. Water would then not be taken up except by capillarity (harmless except in frost) and even then not if the capillary interspaces were completely blocked up.

This then is a tentative definition of a stone preservative against moisture movements. A stone preservative is a substance which in presence of water is preferentially sorbed by the mineral gel, remaining in combination permanently.

Summary

1. A systematic study has been made of the sorption by typical building materials at various degrees of humidity both of water vapour and of other liquids.

2. Certain building stones are shown to be exempt from disintegrating action due to this particular cause, fluctuating humidity.

3. It is shown that the intergrain cement of such stones as sandstone is colloidal whether siliceous or amorphous zeolitic, and an explanation is given of the moisture changes and swelling observed, upon the basis of the micellar hypothesis leading to a suggested definition of a stone preservative against this particular type of disintegration.

4. Parallel results are obtained by staining with dyes.

5. After being heated to 850° sandstone loses its power of sorbing water vapour or dyes.

6. The heat of sorption equals heat of liquefaction in the case of vapour of octane, but is greater in the case of polar liquids.

Department of Physical Chemistry,
The University, Bristol.
December 31, 1926.

A GAGE FOR THE MEASUREMENT OF HIGH VACUA

BY ROBERT E. BURK*

Modern developments in high vacuum technique have made the rapid production of vacua of the order of 10^{-7} mm. of mercury a relatively simple matter, and have given both physicists and chemists powerful experimental methods of attack. However, in applying the new high vacuum technique to chemical problems, there are demands which perhaps come up more frequently than in work in physics; e. g. the chemist can seldom dispense with stopcocks to advantage, he often works with compounds which are decomposed by hot metals, electronic bombardment, etc., and in many of his problems he must evacuate a vessel at frequent intervals.

The standard instrument for the measurement of high vacua is the McLeod gage, but it is not considered practicable below 1×10^{-5} mm. of mercury. For measuring pressures lower than this,[1] the Knudsen gage, the Dushman ionization gage, and the molecular gage have been used. The Knudsen and molecular gages are fragile and difficult to construct. The ionization gage cannot be used in chemically sensitive systems.

The McLeod gage has been extended by Pfund[2] by combining its principle with that of Pirani's hot wire gage. A McLeod gage with electrodes in the capillary, (serving as a rough guide to the pressure of the gas compressed into the capillary), has been used by Klayfeld,[3] and by the writer.[4] Neither of these can be used for measuring the pressure of chemically sensitive gases, and also have other disadvantages.

Description of the New Gage

A gage, shown in Fig. 1, has been constructed which combines the principles of the McLeod gage and the quartz fibre manometer. It can be used with any gas, or any vapor whose vapor pressure is large compared with that of mercury. The gage is easily constructed, and simple in operation. It has no metal parts, can be baked out, and can be calibrated *in situ* without a previous knowledge of its dimensions.

The gage was constructed of Pyrex glass. The volume of V (Fig. 1) was about 330 cc., that of the chamber F, containing the quartz fibres, was somewhat less than 10 c.c. The gas in V was therefore compressed more than thirty times when the mercury was raised from the cut off C to the level L. Two quartz fibres, joined together at the bottom, were used, as suggested by

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* National Research Fellow in Chemistry.

[1] Dushman: "Production and Measurement of High Vacuum" (1922); Newman: "The Production and Measurement of Low Pressures" (1925); Dunoyer: "Vacuum Practice" (1925), translated by J. H. Smith (1926).

[2] Pfund: Phys. Rev., (2) **18**, 78 (1921).

[3] Klayfeld: J. Russ. Phys. Chem. Soc., Phys. part, **57**, 129 (1925); Chem. Abs., 20, 1543 (1926).

[4] Burk: Dissertation, Oxford, May 1926.

Coolidge.[1] This eliminates the complex motions which are sometimes set up in the single fibre, and by trial was found to be well worth while. The fibres were 5.5 cm. in length and 0.068 mm. in diameter.

The fibre chamber F communicated with V by means of a stout tube t (the bore should not be too small), to which was sealed a glass cup A. The cup was insulated with felt. Mercury vapor and other vapors were condensed in t by placing a suitable cooling agent in A. The temperature should be properly chosen so that the vapor can be frozen out to a negligible pressure, or, in case the vapor registers on the instrument with which the gage is compared for purposes of calibration, so that it can be considered as a fixed gas. In this work liquid air and CO_2-ether snow were used. The latter is recommended since at liquid air temperatures the adsorption processes are greatly magnified, and also the vapor pressure of CO_2 falls within the range of usefulness of the gage.[2]

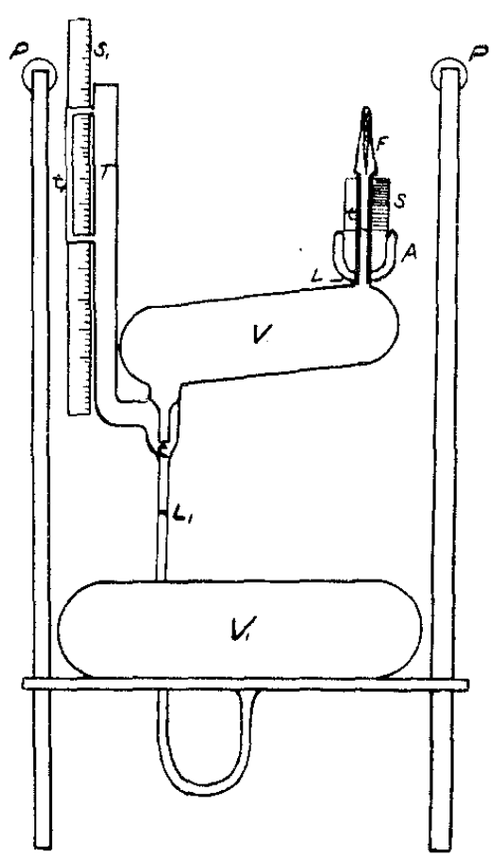


FIG. 1

Due consideration must be given to the processes in the cooled tube t in order to avoid erratic readings. Thus if A is kept at the temperature of ether-CO_2 snow for a continued period when the fibre is used for measuring pressures greater than the vapor pressure of water at that temperature, traces of ice will collect in the tube. If one then attempts to use the manometer for pressures less than the vapor pressure of ice at the temperature of ether-CO_2 snow, water vapor will contribute to the recorded pressures due to the rather slow evaporation of ice at that temperature. Consistent results over the entire range reported were obtained only when the air admitted to the system was that which had stood in a large vacuum bottle, containing 500 grams of phosphorus pentoxide, which was used to back the mercury condensation pump.

The bulb V was connected with a larger bulb V_1, as in the Gaede form of McLeod gage. V_1 was filled with mercury which was heated in vacuo. The tube through which the mercury was introduced was then sealed off with the pump running. V_1 was raised and lowered between two fixed points by means of a mechanical device. (Weights, working over the pulleys P balanced the weight of the mercury). This rendered the operation of the gage very easy. The connection between V and V_1 was made with enamelled rubber tubing, which was evacuated before introducing the mercury. This tubing was sur-

[1] Coolidge: J. Am. Chem. Soc., **45**, 1637 (1923).

[2] Dushman: "Production and Measurement of High Vacuum", 78 (1922).

rounded by larger tubing, and the space between was kept evacuated. For extending the range of the gage, the connection between V and V_1 should be all glass, e. g. a universal joint made from three slip joints. This would minimize evolution of gas from the mercury, which was believed to be a source of error at the highest vacua in this work.

Table I gives the results of the calibration of the gage against a McLeod gage, and the calculation of unknown pressures by its use.

TABLE I

Ave. half life of fibre (sec's)	Recip. of half life $\times 10^3$	Position of mercury	P McLeod mm. $\times 10^6$	P calculated mm. $\times 10^6$
unsteady		lowered	Bubble invis.	(1.5 ± 0.3)
385	2.6	raised		60.0 ± 10
465	2.15	lowered	small bubble	(21.0 ± 1.0)
131	7.63	raised		810 ± 20
385	2.6	lowered	60 ± 10	
60	16.67	raised		2350 ± 20
321	3.12	lowered	90 ± 10	
37	27.0	raised		3900 ± 20
225	4.4	lowered	240 ± 30	
18	55.5	raised		8150 ± 20
184	5.43	lowered	510 ± 30	
89	11.23	lowered	1250 ± 100	
33	30.3	lowered	4500 ± 100	

The values of P (calculated) were obtained by interpolation, using the straight line obtained by plotting the values of P (McLeod) against reciprocal half life of the fibre. The values of P (calculated) in brackets were obtained by dividing the corresponding pressure with the mercury raised by 38.8, the ratio of the volumes of the bulb V to the chamber F. This ratio of volumes is obtained, within the limit of experimental error, when the pressure with mercury raised is divided by the pressure with the mercury lowered in the other cases.

When traces of water vapor were present, the data in Table II were obtained. The vapor pressure of ice at -76.8°C. is added to the McLeod readings.

TABLE II

Ave. half life of fibre (sec's)	Recip. of half life $\times 10^3$	P (McLeod) mm. $\times 10^6 + 0.00075$
129	7.5	950
106	9.43	1150
92	10.86	1600
77	12.98	1950
49	20.40	2630
45	22.20	2950
28	35.70	5450
20	50.00	6750
16.5	60.55	8850

The mercury was lowered in each case, and the McLeod readings are subject to variations similar to those mentioned in the previous table.

The quartz fibre manometer was originally studied by Haber and Kerschbäum,[1] who give the following equation for the relation between the pressure, p, and the time, t, for the amplitude of the vibration to decrease by half

$$b = (\Sigma [p\ M^{1/2}] + a)t$$

a and b are constants. $\Sigma [p\ M^{1/2}]$ represents the sum of the products partial pressure $\times$ (molecular weight)$^{1/2}$ for all the gases present.

With the bifilar manometer used in the present experiments, a straight line was obtained when p was plotted against $1/t$, over the pressure range 6×10^{-5} mm. of mercury to 8.85×10^{-3} mm. of mercury, as predicted by the above equation.

The readings of the new gage were somewhat variable at the highest vacua, and in such a direction as to indicate slight adsorption on the walls of the vessel, and occasional liberation of gas, presumably from the mercury. The gage could be improved by making the connection between V and V_1 all glass, as previously mentioned, and by placing V and F in thermostats. The ratio of the volume of V to that of F could easily be increased to 300. The range of the instrument could thus be extended to 1×10^{-7} mm. of mercury without inconvenience.

The instrument can be used as an ordinary McLeod gage from $p = 0.00885$ mm. of mercury, (where the half life of the quartz fibre becomes small), to the range of the ordinary manometer. The side tube t, for equalizing capillary depression, and the scale S would then be used, as in the usual McLeod gage.

By measuring the difference in level between the mercury in V_1 and in the tube T, using the scale S_1, or a cathetometer, the gage can be used for measuring pressures up to atmospheric. A single set up of this type may thus be employed for measuring pressures over the range atmospheric pressure to 1×10^{-7} mms. of mercury.

Description of Stopcocks employed

Connections to the mercury pump etc. were made through two way stopcocks of the type shown in Fig. 2, which can be used either with a lubricant, or mercury sealed with no lubricant. The bore in these stopcocks was 14 mm. in diameter $\times$ 2 mm. in length. The enormous saving in time of evacuation resulting from the use of such stopcocks is apparent when its dimensions are substituted in Dushman's formula.[2]

$$Q = \frac{p_2 - p_1}{\left[\frac{2.394\ L}{d^3} + \frac{3.184}{d^2}\right] \sqrt{\frac{M}{83.15 \times 10^6 T}}}$$

[1] Haber and Kerschbaum: Z. Elektrochemie, **20**, 296 (1914).

[2] Dushman: Int. Critical Tables, **1**, 91 (1926).

Let $p_2 - p_1 = 0.01$, and T = 295; then Q, the amount of gas flowing through the bore in cc. per sec is 125 when the above dimensions of the large bore stop cocks are substituted, and 0.714 when the dimensions of ordinary mercury seal stop cocks are substituted e.g. 2 mm. bore, 17 mm. long. The value 0.714 would again be very much reduced by clogging with grease, which is so difficult to avoid with small-bore stopcocks.

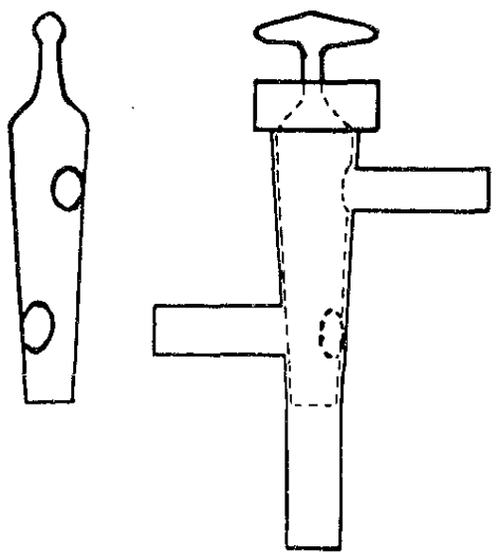


FIG. 2

Summary

A gage combining the principles of the ordinary manometer, the McLeod gage, and the quartz fibre manometer has been described, which is capable of measuring pressures from several decimeters of mercury to 1×10^{-7} mm. of mercury. It has been tested for pressures down to 1×10^{-6} mm. of mercury.

A two-way stopcock has been described which has been found to be very useful in working with high vacua.

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Baker Laboratory of Chemistry,
Ithaca, New York.

THE BASIC VISCOSITY OF ICE-CREAM MIXES

BY ALAN LEIGHTON AND OWEN E. WILLIAMS*

The purpose of this paper is to demonstrate that there exists in normal ice-cream mixes a measurable basic viscosity, that is, a viscosity independent of changes in mechanical structure which take place when the mix is allowed to stand. This paper also shows that the change in value of this basic viscosity *with variation in water concentration, at constant temperature,* follows closely a modified form of the equation given by Arrhenius,[1] $\log \eta = \Theta c$.

When freshly prepared ice-cream mixes are allowed to stand at low temperatures they show a marked increase in viscosity. In commercial practice freshly prepared mixes are held for a period of at least twenty-four hours before being frozen, as it is the common belief that this increased viscosity is desirable. This procedure is known technically as ripening, and is sometimes called 'aging.'

A study of the viscosity of such a ripened mix shows that any mechanical agitation reduces the viscosity, and also that, with successive passages of the mix through a viscometer of the Ostwald type, the time required for the passage of the liquid gradually decreases to a value dependent upon the instrument itself. These phenomena are aptly described in an abstract[2] of a paper by Weissenberger[3] dealing with the structure of disperse systems. Portions of this abstract are quoted:

"Dispersoids, more particularly emulsoids, whose concentration exceeds a certain limit, tend to form uniform secondary aggregates of the primary particles of the disperse phase, probably as the result of a special hindering of the free movements of the particles. The primary particles, which are ultramicroscopic aggregates of molecules, are very stable and reproducible. . . . In turn, secondary structures may unite to form aggregates of still higher orders. . . . These structures of higher orders are easily broken down, for example, by mechanical agitation, by shaking, or by forcing the solution through capillaries. If the viscosity of such an emulsion is measured in an Ostwald viscometer, it is bound to fall off with successive passages through the capillary until a constant value is obtained, the magnitude of which depends upon the size of the capillary. If the dispersoid is then allowed to rest, the viscosity slowly increases again as the structures of higher order are again formed."

From the foregoing it is apparent that as soon as ripened ice-cream mix enters the freezer the dashers will reduce the existing viscosity. If the in-

*Dairy Research Laboratories, Bureau of Dairy Industry. United States Department of Agriculture.

[1] Medd. Nobel Inst., **8**, No. 13, 1-20 (1916), J. Chem. Soc., **112** II, 130.

[2] Chem. Abs., **15**, 3777 (1921).

[3] Kolloid-Z., **29**, 113-24 (1921).

creased viscosity of this ripened mix is due to the development of a mechanical structure, when this structure is broken down the viscosity obtained should be a basic value, independent, within certain limits, of the rate of stirring.

For clearness, this paper will refer to the viscosity of the unagitated ripened mix as the *apparent viscosity* and to that obtained upon agitation as the *basic viscosity*. The existence of this basic value was demonstrated as follows:

An unflavored ice-cream mix was made up, as is customary, from unsweetened evaporated milk, cream, cane sugar, and water, with the addition of a small amount of gelatin. This mix was pasteurized at 63°C., for one-half hour, homogenized at a pressure of 2500 pounds per square inch while still hot, immediately cooled, and stored for a day at a temperature of about 2°C. The total solids content of this mix was 36.3 per cent. Its viscosity when freshly prepared (measured at 0° C.) was found to be 9.11 centipoises (cp). The next day the apparent viscosity was >50 cp. A portion of the mix was then run into a horizontal-type, brine-cooled freezer of six gallons capacity. The freezer was filled completely so that air could not be whipped into the mix by the dasher. When the mass was brought to a temperature of 0°C., the dashers were started at a speed of 130 R. P. M., the normal speed of the freezer. At intervals of five minutes for a period of one hour samples were drawn from the freezer into small flasks, packed with snow, and carried to the viscometer, which was immersed in a constant temperature bath held at 0°C. The viscosity value was found to be constant for this period of time at 36.31 cp. The basic viscosity was therefore reached quickly in the freezer. To check this value, portions of the same mix were placed in small side-necked filter flasks, the flasks evacuated of air at the pump and then shaken on a shaking machine of two-inch stroke at a rate of about 275 strokes per minute for various periods up to one hour, care being taken to prevent the mix warming appreciably. The same constant basic viscosity value was obtained as in the freezer. As a third check, about 400 cubic-centimeter portions of the mix were placed in 600 cubic-centimeter beakers, set in snow, and stirred rapidly with a small laboratory stirrer. The basic viscosity of these samples remained constant up to periods of one hour at the same value given by the other experiments. These results have been repeatedly obtained, although it has been found that the structural viscosity of more concentrated mixes could not be completely broken up by the shaking machine or the stirrer.

Now Arrhenius, has shown for colloidal solutions:

$$\log \eta = \Theta c$$

where η is the viscosity (in centipoises), c the concentration (molecular concentration, or with substances of high molecular weight, parts per 100 of solvents), and Θ a constant. This equation is that of a straight line passing through the origin. In other words, if the concentration of the solution under investigation becomes zero, the logarithm of viscosity is zero, or the viscosity value of the solvent is one, that of water at 20° C. The experiments herein described were carried out at 0°C where the viscosity of water is 1.796. It seems best therefore to express the equation as

$$\log \eta = \Theta c + k.$$

where k is a constant and, theoretically, should equal log 1.796 or .2544.

As further proof that there is a true fundamental viscosity, measurements were made of the basic viscosity of ice-cream mixes of varying water content. Since it can be shown[1] that probably not more than half the water of an ice-cream mix is ever changed to ice in the freezer, the limiting concentration was that of a two-to-one mixture. Three mixes of different relative fat, milk solids and sugar contents were chosen, as shown in Table I. In the case of mix No. 1 four separate portions, of the different water concentrations in-

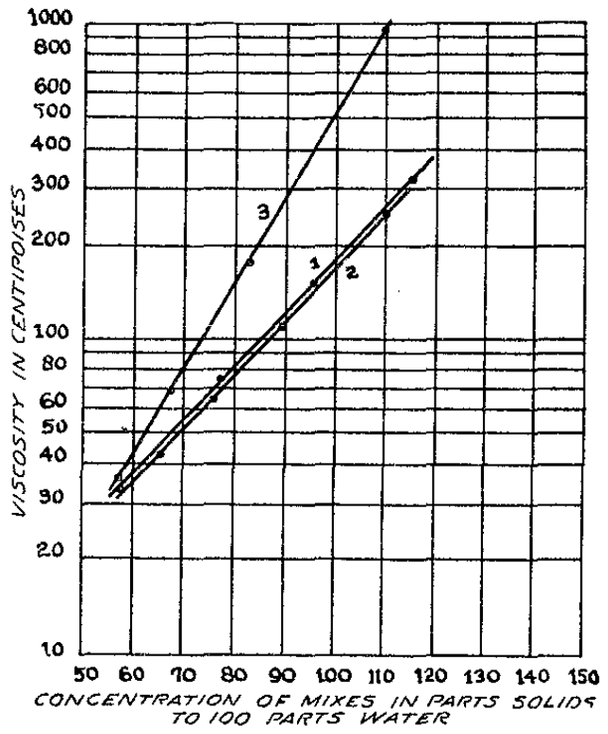


FIG. 1
Logarithmic plotting of basic viscosity against direct plotting of the concentration of ice-cream mixes.

dicated, (a, b, c, and d) were prepared directly. These were stirred separately in the freezer at 0°C. until a constant value for basic viscosity was obtained. It took 90 minutes to reach the basic value of sample d.

In the case of mixes No. 2 and No. 3 only the most concentrated sample (d) was prepared. After the basic viscosity had been determined for this concentration (d), the mix was drawn from the freezer, weighed and diluted with cold water to the next concentration (c) and the process repeated to the lower concentrations (b and a). The table gives not only the concentrations as determined by analysis but also the basic viscosities and the calculated value of Θ, the Arrhenius constant, as well as the constant k. In Fig. 1 the viscosities are plotted logarithmically against the actual concentration.

[1] Leighton: "The Calculation of the Freezing Point of Ice Cream Mixes." In press, J. Dairy Sci.

TABLE I

Basic Viscosity and Arrhenius' Constant (Θ) of Ice-Cream Mixes of Varying Composition and Concentration

No. 1. Composition	Parts	No.	Conc'n*	Visc (cp)	Θ	K
Fat	12.0	a	57.6	36.21	.01655	.6039
Sugar	14.0	b	76.8	77.18	.01670	"
Milk Solids		c	96.0	147.70	.01630	"
Not Fat	10.0	d	115.2	326.50	.01658	"
Gelatin	.3					
	36.3					
Water	63.7					

No. 2. Composition	Parts	No.	Conc'n*	Visc (cp)	Θ	K
Fat	8.0	a	64.5	43.34	.01660	.5663
Sugar	14.0	b	75.2	65.04	.01660	"
Milk Solids		c	89.4	110.5	.01652	"
Not Fat	12.0	d	110.0	246.8	.01660	"
Gelatin	.3					
	34.3					
Water	65.7					

No. 3 Composition	Parts	No.	Conc'n*	Visc (cp)	Θ	K
Fat	16.0	a	56.3	35.9	.02600	.0910
Sugar	14.0	b	66.6	70.5	.02637	"
Milk Solids		c	82.8	175.4	.02600	"
Not Fat	6.0	d	109.5	881.4	.02605	"
Gelatin	.3					
	36.3					
Water	63.7					

*Expressed in number parts total solids to 100 parts water.

From the table and plot it is seen that straight line curves result, showing, as would be expected from the Arrhenius formula, that there is a definite relation between the logarithm of the viscosity and the concentration of the mixes. The viscosity values calculated for zero concentration (the values of *k*) vary from the theoretical. These variations are probably to be explained by the fact that in the mixes under experiment the weight concentration is only a rough approximation of the true molecular concentration. It seems reasonable, therefore, to conclude that the basic viscosity is a true fundamental value.

We have already stated that the viscosity of a freshly prepared mix has a lower value than the basic viscosity of the mix that has stood overnight. (9.11 cp to 36.21 cp). Additional experiments have shown that the basic viscosity of a mix shows no further change after standing for one week at

5° C., although, as would be expected, there is a marked increase in the apparent viscosity. When the mix is pasteurized it is, of course, heated above the melting point of the fats. If these do not harden rapidly upon cooling, it would be expected that the viscosity of the fresh mix would be low. The basic viscosity of a mix standing one day would therefore be higher than the viscosity of the freshly made mix. This increase can be explained in only one other way, which is to assume, at this stage, a certain degree of hydration of the milk solids, but Dahle and Caulfield[1] have measured the "bound water" of an ice-cream mix when freshly prepared and at intervals of 24, 48, and 72 hours. They find a constant low value. They conclude that the hydration of the protein of an ice-cream mix is complete before the ripening process is begun. If this is the case then the increase in the basic viscosity of the mix on standing, over that of the freshly prepared mix, must be due, not to the hydration of the protein, but to the solidification of the fats. The apparent viscosity must be the result of mechanical structure.

Conclusions

The existence of a measurable basic viscosity of ice-cream mixes has been demonstrated.

The change of value of this basic viscosity with concentration has been shown to follow the Arrhenius equation.

[1] Unpublished data, kindly transmitted to authors of this paper.

5 - 463

THE COALESCENCE OF AN UNFILTERABLE PRECIPITATE OF BARIUM SULFATE*

BY H. M. TRIMBLE**

Introduction

It has long been known that a precipitate which has just been thrown down from solution, and which is so fine as to pass through an ordinary filter, may be made filterable by digesting it for some time at an elevated temperature in contact with the mother liquor from which it was separated. Ostwald[1] was apparently the first to advance an explanation for this phenomenon. Under these conditions, he states, the smaller particles dissolve and the larger ones grow by deposition, so that finally a precipitate results which is sufficiently coarse to filter well. This explanation was an application of the principle enunciated by Sir William Thomson,[2] later Lord Kelvin, according to which the vapor pressure or solution pressure of a substance in the form of very small particles varies inversely as the size of its particles. Some work (soon to be published), carried out by the author with Professor S. Lawrence Bigelow indicated that, while it is undoubtedly true that the vapor pressure of a small particle is greater than that of a larger one, yet this difference is vanishingly small for particles of measurable size. It was found, too, that any transfer of material from smaller to larger particles due to such difference is exceedingly slow. By analogy it seemed that the rate at which larger crystals of a nearly insoluble substance will grow at the expense of smaller ones in contact with its solution must be very low; probably too low to account for the coalescence of precipitates as it occurs in ordinary analytical practice.

Evidence is not wanting to show that this is, indeed, the case. G. A. Hulett,[3] in the course of a study of this very matter, added three grams of very finely pulverized gypsum to 250 cc. of a solution which had been saturated over large plates of this material and agitated the preparation gently at constant temperature. The concentration of the dissolved electrolyte was determined from time to time by measuring the electrical conductivity of the solution. The small particles were, on the average, about 0.3 microns in apparent diameter at the start of the experiment. The conductivity rose to a maximum almost immediately, and then fell slowly. At the end of 48 hours it had fallen nearly to the conductivity of a normally saturated solution; but it was only after nine days that this value was actually reached. Parallel

* Contribution from the Chemistry Laboratory of the University of Michigan.

** The work presented in this paper is taken from a dissertation presented in partia fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan. The investigation was carried out under the direction of Professor S. Lawrence Bigelow.

[1] W. Ostwald: "Analytische Chemie" pp. 14, 22 (1894).

[2] W. Thomson: Proc. Roy. Soc. Edinburgh, 7, 63 (1870).

[3] G. A. Hulett: Z. physik. Chem., 37, 385-406 (1901); 47, 357-367 (1904).

with this decrease of the conductivity, which indicated a decrease in the concentration of the solution, went the disappearance of the smallest particles. At the end of nine days they had disappeared completely, and the smallest particles then present were approximately two microns in diameter. Hulett concluded that above this size, the solubility of gypsum is no longer a function of particle size. It is noteworthy that equilibrium was approached very slowly during the latter part of this experiment. If we accept the explanation of coalescence which Ostwald advanced, it follows that the rate of elimination of the last of the smaller particles is very low.

Hulett found in similar experiments that barium sulfate behaved in the same manner as did gypsum. In particular he found that, at 25°C., its solubility is no longer a function of the size of its particles if these latter are larger than about 1.8 microns in diameter.

Von Weimarn[1] found that colloidal barium sulfate is converted to regular crystals in the course of time. Thousandth-normal solutions of barium thiocyanate and manganous sulfate were mixed in the cold, and the precipitate was allowed to stand quietly in contact with its mother liquor without stirring or shaking. His description follows:

"During the first few hours after the appearance of the opalescence the greater part of the precipitate consists of particles which seem to be spherical under the highest magnifications of the microscope. After twelve hours the part of the precipitate which has settled upon the bottom of the vessel consists of tiny crystals in the form of parallelopipeds of different sizes, and of aggregates of spherical particles (as seen under a magnification of 1500 times). After a month it is readily seen that the crystals have grown; but the aggregates of spherical particles still constitute an important part of the precipitate. It requires a half year for the aggregates to disappear almost completely; and at that time the precipitate consists of characteristic barium sulfate crystals."

The individual units in the aggregates of spherical particles cannot be seen in the photographs as given. It seems certain that they were very small.

If the colloidal material of this experiment was amorphous barium sulfate, it constituted an unstable phase in the precipitate. The difference in solution pressure between an unstable and a stable form of this substance is certainly greater than any such difference between particles of comparable sizes in either phase. The transfer of material in a system containing these two phases should be more rapid than in one which contains only crystals of different sizes. But von Weimarn holds that all matter, even in the colloidal state, is crystalline. If this is true, the system with which he worked was the same in nature as that which we are considering. The question cannot be decided by microscopic examination, since very small particles of any kind show up as tiny discs of light, quite without distinguishing features. No matter which view we take, however, the experiment furnishes direct

[1] P. P. von Weimarn: Kolloid-Z., **3**, 289-90 (1908).

evidence that the growth of larger particles of barium sulfate at the expense of smaller ones, at room temperature and without stirring, is a very slow process.

But for lack of space, various other observations of this kind might be cited. In every case, so far as the author is aware, the changes studied took place at or near room temperature. But digestions for the purpose of rendering an unfilterable precipitate filterable are invariably carried out at elevated temperatures. It seemed worth while, then, to determine whether the same results would be found at these higher temperatures.

Experimental Part

Obviously a precipitate can be made filterable by digestion only if all particles small enough to pass through the pores of the filter can be eliminated in this way. The average size of the pores in ordinary thick filter paper has been found to be[1] about 3.3 microns. This value was calculated from the permeability of this paper to water, and may or may not indicate the magnitude of the actual maximum pore size. A number of experiments were run, accordingly, to determine the size of the largest particles which will pass through such filter papers as are commonly used in quantitative analysis. Finely pulverized barium sulfate was suspended in water and this suspension was poured into filters made up in the usual way using three well-known kinds of filter paper. The part of the precipitate which passed through was collected and its particles were examined under the microscope. In every case particles as large as three microns in diameter were not at all uncommon, and some which were as large as four microns were found. The maximum pore sizes, then, must be very much as calculated from the permeability to water. It seems safe to set somewhat more than four microns as the size of the smallest particles which will certainly be retained by ordinary quantitative filter paper.

But a filter is by no means a sieve. Filter paper is a colloidal material which is usually negatively charged. As such it tends to hold barium sulfate particles of any size, since they are positively charged when prepared, as in quantitative analysis, by precipitation from dilute acid solutions of sulfates by the addition of barium chloride. Due to this and other causes its pores soon become clogged and its efficiency is thereby increased. Filters of other materials might be used in separating particles of different sizes; but at the best the retaining power of any given filter is only very imperfectly reproducible. While, then, filterability serves as a convenient practical criterion as to particle size, it is not a very certain or useful one. The direct measurement of particles with a microscope, using a filar micrometer, is much better. The unavoidable error which is involved may be reduced to a minimum by measuring a large number of particles from each precipitate which is examined. This method was used in the present study, supplemented by numerous tests as to filterability using filters of ordinary quantitative filter paper.

[1] "Third Report on Colloid Chemistry." Brit. Ass. Adv. Sci., L. p. 68 (1920).

Barium sulfate is perhaps more frequently digested to render it filterable than any other precipitate which is handled in quantitative analysis. Its low solubility should make the growth of larger particles at the expense of smaller ones very slow. But it is found in practice that a few hours digestion at a high temperature in the presence of a small amount of hydrochloric acid, without stirring, will render a precipitate of this substance readily filterable, provided it has been prepared in the proper manner. For this reason it seemed the most suitable substance for study. It was used in most of the experiments which are described below. The results have been confirmed, however, by experiments in which barium chromate, lead chromate, lead sulfate and calcium oxalate were used. The experiments had for their purpose to determine whether particles of these substances smaller than about four microns in average diameter can be eliminated from precipitates containing them by digestions such as are carried out in ordinary quantitative analysis.

Rhombohedral crystals of barium sulfate about ten to twenty five microns in length were prepared by slow addition of barium chloride solution to a hot dilute solution of sulfuric acid containing a small amount of hydrochloric acid. Small particles were prepared for the first experiments by crushing this material in an agate mortar, suspending the powder in a large quantity of water and pouring off the suspension which had not settled out after standing quietly for one or two minutes. These particles were recovered by allowing the suspension to settle for about an hour and then pouring off the supernatant liquid. This left a heavy suspension which was used at once in an experiment. It was impossible to filter these precipitates clear. As measured under the microscope the individual particles were found to be between one and four microns in diameter, the smallest ones being vastly in the majority. Particles smaller than one micron were few.

About one-tenth gram of larger rhombohedral crystals was added to a portion of this suspension which contained one fourth to one half gram of material. The volume was then made up to about 500 cc., hydrochloric acid was added, and the preparation was divided into approximately equal portions after stirring it up. One portion was then allowed to digest at about 95° to 100°C. without stirring. The other was heated under the same conditions, except that it was stirred during the progress of the experiment by means of a mechanical stirrer. Water and a little hydrochloric acid were added from time to time as needed to replace the liquid lost by evaporation. Nine experiments were run in this manner. The precipitates which were digested without stirring filtered clear after two to four hours in every case. Microscopic examination showed that the small fragments which were introduced at the start had, in these experiments, formed aggregates. Their average size remained almost unchanged. The other preparation which had been digested with stirring would not filter clear even after three days or more. Microscopic examination showed that the smallest particles had disappeared during this digestion. No particles smaller than about two microns in diameter could be found in the precipitates. The size of the larger rhombohedral crystals was not appreciably changed in any case.

In ten similar experiments suspensions of barium sulfate which had been prepared by mixing normal solutions of barium chloride and sulfuric acid in the cold were used. Such volumes of the solutions were taken that about one gram of barium sulfate was thrown down. The particles which formed were all very small; none of them being larger than one micron in apparent diameter. The larger rhombohedral crystals which were present during the digestions did not change appreciably in size. The portions which were digested without stirring coalesced more slowly than before; but five to ten hours sufficed to render the precipitates filterable in every case. At this stage the particles were again aggregated together. The aggregates were all made up of unit particles two microns or less in diameter. In the portions which were digested with stirring all the smallest particles disappeared, so that at the end of three days the smallest ones present were two microns or more in diameter. The precipitates could not be filtered clear in any case, though four digestions were carried on for two weeks in the hope of attaining this end. It was, of course, impossible to determine whether or not the total amount of fine precipitate had diminished. Even at the end of two weeks digestion the smallest particles present were still about two microns in diameter

Numerous experiments were carried out in the attempt to grow crystals at the expense of finely divided and apparently amorphous barium sulfate at elevated temperatures. The precipitates were prepared by mixing in the cold equivalent volumes of barium chloride and sulphuric acid. The concentrations of these solutions varied between one hundredth normal and twice normal. The amount of the precipitate at the start, the concentration of hydrochloric acid at the start and the time of digestion were all varied between rather wide limits. The digestions were carried out both with and without stirring, but large crystals were not introduced in any case. The precipitates were examined from time to time with a microscope, using a magnification of 1000 diameters, but no crystals which were recognizable as such were ever found. The largest particles before digestion were less than one micron in diameter. After digestion for some days they were between two and three microns in diameter, on the average. Those precipitates which were digested without stirring became filterable after a day or two in some cases. In others they could not be made filterable. None of those which were digested with stirring were rendered filterable.

Ammonium acetate and sulfuric acid were introduced in a number of experiments instead of hydrochloric acid. Digestions were carried out both in the presence and in the absence of large rhombohedral crystals of barium sulfate. It was hoped that these solvents might aid in the growth of larger particles at the expense of smaller ones. This hope was realized, in that all particles smaller than about two microns disappeared after a few days digestion. Particles of this size, however, could not be eliminated by further digestion.

It seemed that any loss of matter by the smaller particles to larger ones in these experiments might be revealed if the total quantity of the former was very small. In some further experiments, therefore, just enough barium

chloride and sulfuric acid were added to distilled water to give a faint opalescence. The particles which were present at this stage were not measured. Large rhombohedral crystals were then introduced and the preparations were digested hot, with stirring. Hydrochloric acid, ammonium acetate and sulfuric acid were introduced in different experiments as solvents. After two or three days digestion the precipitates were collected and studied. The very small particles which at first formed the opalescence had disappeared and in their place were many particles about two microns in diameter. The small particles were not removed entirely, as might have been expected. The findings of the earlier experiments were thus confirmed.

Discussion of Results

This work shows that particles of barium sulfate larger than two microns in apparent diameter cannot be made to go over to yet larger ones, even by protracted digestion at a high temperature. Measurements of large crystals before and after digestion, too, showed that their growth is inappreciable. It follows, then, that the coalescence of an unfilterable precipitate which renders it filterable cannot be explained in terms of the growth of larger particles at the expense of smaller ones. But we must still account for it, for the change undoubtedly takes place. The fact that, on digestion without stirring, aggregates form; while they do not form when the digestion is accompanied by stirring shows the way to the answer. In view of all the facts the best explanation seems to be as follows: The precipitated particles when allowed to settle come into intimate contact with one another and form aggregates which adhere rather firmly. As the digestion proceeds barium sulfate, either from the still supersaturated solution or from the dissolving of very small particles, deposits upon these aggregates and cements them together. This effect is enhanced when the solution is allowed to cool. In this way large bodies which will not pass through the pores of a filter are formed.

On the other hand, when the digestion is accompanied by stirring all the crystals present grow alike at the expense of any material which may be separating from solution. There is no opportunity for cemented aggregates of crystals to form. Thus, while larger crystals do grow at the expense of smaller ones, if the latter are less than about two microns in diameter, the amount of such growth is very small; so small, indeed, that it could not render filterable a precipitate which is otherwise unfilterable.

Summary

The results of this study show that the solution pressure of barium sulfate at about 100°C. ceases to be a function of particle size for particles larger than about two microns in diameter. The coalescence of barium sulfate precipitates on digestion which renders them filterable cannot be adequately explained in terms of the growth of large particles at the expense of smaller ones. It is brought about, rather, by the collection of particles into relatively large aggregates, followed by the cementing together of the unit particles in the aggregates.

STUDIES ON THE SYSTEM LIME-ALUMINA-SILICA. THE COMPOSITION $8CaO + Al_2O_3 + 2SiO_2$

BY W. C. HANSEN, W. DYCKERHOFF, F. W. ASHTON AND R. H. BOGUE[1, 2]

Introduction

Jänecke[3] in 1912 reported that he had obtained a compound of the composition $8CaO \cdot Al_2O_3 \cdot 2SiO_2$ in the ternary system CaO-Al_2O_3-SiO_2. Rankin and Wright[4] disagreed with him and in their complete study[5] of the system found no evidence to substantiate his belief. Wetzel[6] studied polished sections of Jänecke's preparations by etching with acids and concluded that the phase considered by Jänecke as the $8CaO \cdot Al_2O_3 \cdot 2SiO_2$ compound was a primary phase separating out of a glass and, therefore, did not have the composition of the preparation *i.e.*, $8CaO + Al_2O_3 + 2SiO_2$. The descriptions of this phase given by Jänecke and by Wetzel indicated, however, that it was different from any described by Rankin and Wright.

Upon making a comprehensive study of the system CaO-Al_2O_3-SiO_2 one of us[7] found a crystalline phase that differed in appearance from those ordinarily found[8] in portland cement or preparations of CaO, Al_2O_3, and SiO_2. This phase was formed by heating the mixtures in an oxyhydrogen flame, a method described in a previous publication.[9] A study of the new phase was made and the conclusion reached that it had a composition of $8CaO + Al_2O_3 + 2SiO_2$. The results of this study, however, agreed with those of Jänecke only as to the composition of this phase. The conditions for the formation of the "compound" and the other properties associated with it were reported to be different from those attributed to it by Jänecke.

The phase in question was found also by the rest of us,[10] using the method employed by Dyckerhoff. A study of this phase gave results which seemed, however, to be opposed to the existence of the ternary compound.

An opportunity presented itself for the four of us to work together for a few weeks, and the results of this cooperative investigation are presented in the present report.

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[1] Published by permission of the Director of the National Bureau of Standards of the U. S. Department of Commerce.

[2] Paper No. 6 of the Portland Cement Assoc. Fellowship at the Bureau of Standards.

[3] Z. anorg. Chem., **73**, 200 (1912); **74**, 428 (1912); **76**, 357 (1912); Protokoll Ver. deut. portland cement Fabrikanten, **36**, 273 (1913); **37**, 160 (1914); Z. anorg. allgem. Chem., **93**, 271 (1915); Zement, **14**, 272 (1925).

[4] Z. anorg. Chem., **75**, 63 (1912).

[5] Am. J. Sci., **39**, 1 (1915).

[6] Protokoll Ver. deut. portland cement Fabrikanten, **35**, 217 (1912); **36**, 347 (1913); **37**, 145 (1914).

[7] W. Dyckerhoff: Dissertation (1925), University of Frankfurt. Cf. Zement, **13**, 681 (1924); **14**, 3, 21, 61, 103, 120, 140, 175, 200 (1925).

[8] Crystals of this kind are occasionally found in commercial cements.

[9] W. Dyckerhoff: Zement, **13**, 455-467 (1924).

[10] Unpublished work.

Experimental Part

Materials used.—The raw materials used in this investigation were calcium carbonate, alumina, silica and ferric oxide. The chemical analysis[11] of each is given below:

	Calcium Carbonate	Alumina	Silica	Ferric Oxide
CaO	55.55	0.02	0.02	——
CO_2	43.63	——	——	——
Al_2O_3	0.01	98.35	0.50	——
SiO_2	0.03	0.00	99.37	——
Fe_2O_3	——	0.10	0.03	99.15
FeO	——	——	——	nil
MgO	0.07	0.08	——	——
SO_3	0.00	0.00	——	nil
P_2O_5	0.02	——	——	——
Cl	0.04	0.01	——	——
Loss on ignition	43.97	1.55	0.11	0.93

Heat treatments.—The preparations were made by first mixing the raw materials in the proper proportions on paper and decarbonating in an electric muffle furnace in a platinum dish. The mixture was then made into a stiff paste with water on a glass plate and kneaded for about thirty minutes to insure homogeneity. The paste was rolled on waxed paper into rods about the size of a lead pencil and these when dry were held in the oxy-hydrogen flame until a good sized drop formed. This drop was melted off and allowed to fall on platinum foil and cool in the air. Several grams of the $8CaO + Al_2O_3 + 2SiO_2$ composition were prepared in this way and used for the examinations and experiments described below.

A number of the drops were powdered and a sample analysed to ascertain if the ratio of the components had remained constant during the burning. The results of this analysis[1] are compared below with the theoretical composition.

	Analysis of drops per cent	Theoretical $8CaO + Al_2O_3 + 2SiO_2$ composition per cent
CaO	66.73	66.76
Al_2O_3	15.25	15.23
SiO_2	17.86	18.00

Thin sections were made of some of the drops and examined with a petrographic microscope. Fig. 1 is a photomicrograph of one of these sections taken under crossed nicols. The fiber-like structure illustrated in this figure was found to be very abundant in all of the drops examined indicating that it might be due to a ternary compound. Some of the drops were powdered and examined microscopically; glass and CaO could then be identified. Com-

[11] Analyses by H. C. Strecker.

plete optical measurements were not obtained on the fibers because of the difficulty of finding good individual crystals but the bi-refraction and mean index were very close to the values given by Wright for $3CaO \cdot SiO_2$.

This indicated that the aggregates might be $3CaO \cdot SiO_2$. If this were the case, two other phases, $2CaO \cdot SiO_2$ and $3CaO \cdot Al_2O_3$, should appear if the preparations were treated in such a way as to bring about equilibrium.

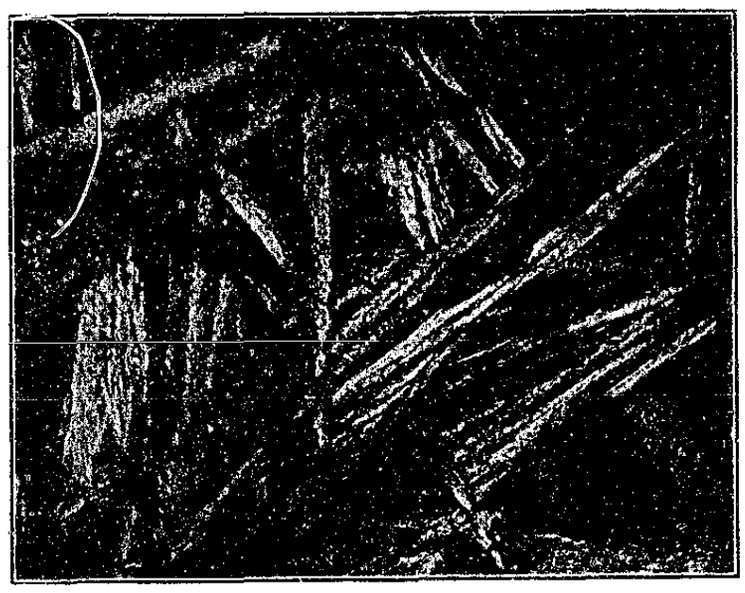


FIG. 1
Composition 8 CaO + Al O_3 + 2 SiO_2
Nicols crossed, × 85
Characteristic fiber-like structure observed in the drops prepared in the oxyhydrogen flame.

From the diagram given by Rankin and Wright,[5] page 40, a part of which is given in Fig. 2, it may be seen that in such a composition $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$ and $3CaO \cdot Al_2O_3$ exist together at equilibrium at temperatures up to 1455°.[12] At that temperature the first liquid appears. Therefore, to obtain such an equilibrium and complete crystallization as rapidly as possible a temperature just below 1455° should be used.

A treatment which would establish equilibrium if the crystals were $3CaO \cdot SiO_2$ should tend to establish equilibrium and cause the preparations to become more nearly homogeneous if they were a ternary compound.

The following experiments were performed in an effort to establish equilibrium in these preparations.

(1) Two drops were wrapped in platinum foil, suspended in the quenching furnace[13] and heated to about 1600° at which temperature they were held for one hour. They were then cooled to 1450° during one and one-half hours and held at 1400°-1450° for one and one-half hours.

[12] All temperatures discussed in this paper are in degrees centigrade.

[13] See Hansen and Bogue: J. Am. Chem. Soc., **48**, 1261 (1926) for a description of this furnace and temperature measurements.

The two drops fused together during the treatment. The charge was sawed in two with a diamond saw, a thin section and powder were examined microscopically but no marked changes could be observed.

(2) A charge of powdered drops was heated in the same way to about 1600°, held there for one hour, and cooled to 1450° during one hour. It was

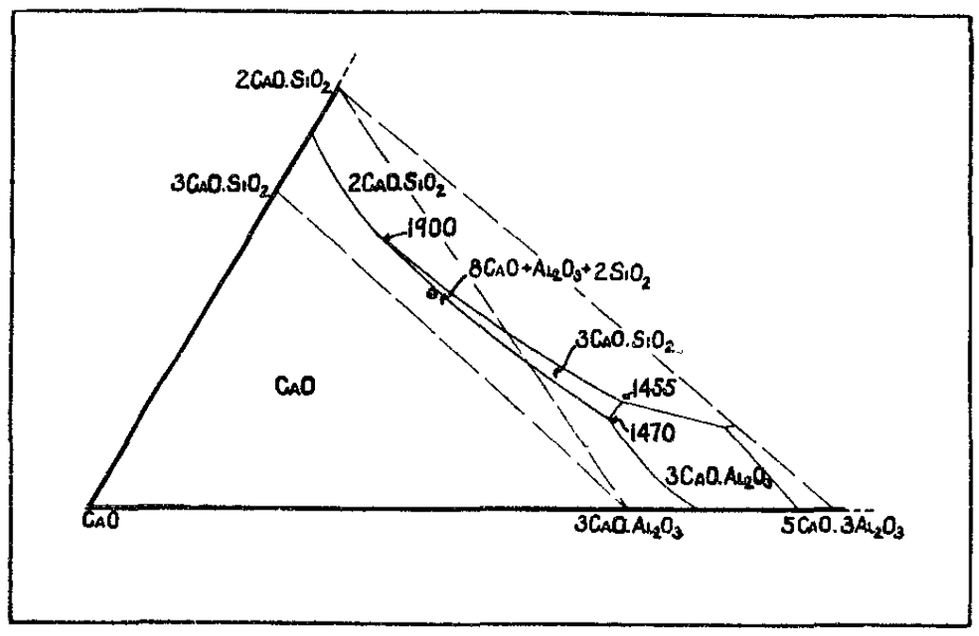


FIG. 2
Section of diagram of System $CaO - Al_2O_3 - SiO_2$ (Rankin and Wright).

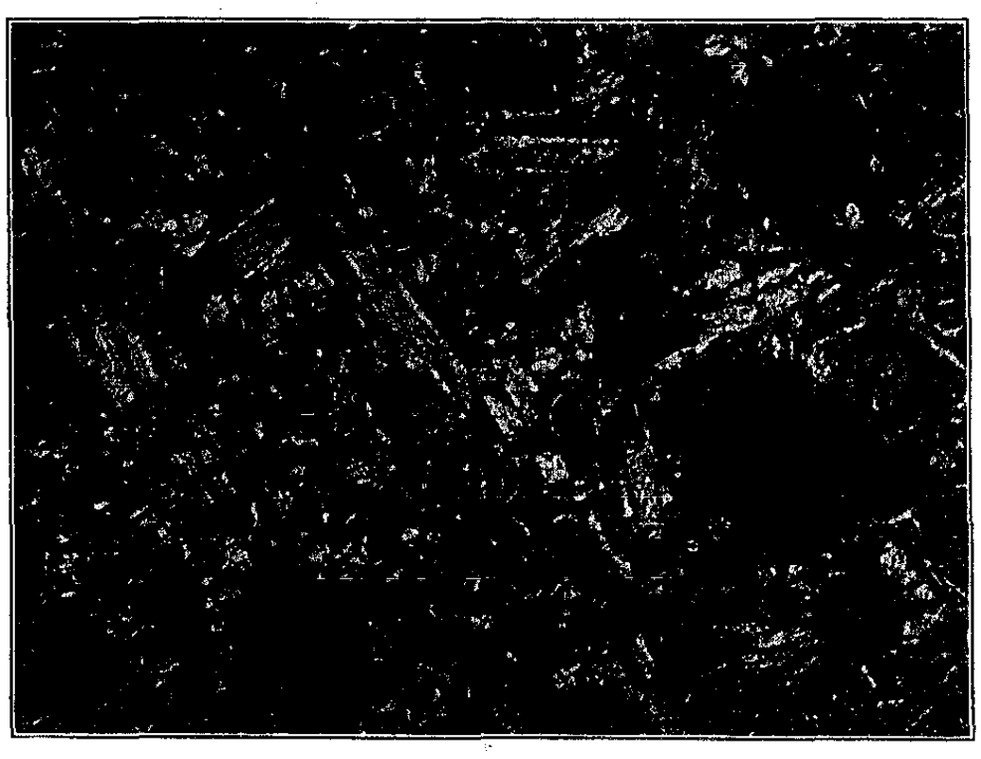


FIG. 3
Nicols crossed, ×95
Photomicrograph of charge 2, which was held at 1400°-1450° for 15 hours. Note the higher birefraction of edges of large crystals showing the formation of 2 $CaO.SiO_2$.

then held at 1400°-1450° for fifteen hours. In this charge the amount of the fibrous aggregates had decreased as shown in the photomicrograph of a thin section in Fig. 3. The edges of many of the large crystals that remained had a much higher birefraction than did their interior as is brought out clearly in the figure. This indicated that the liquid present during the treatment was reacting with the aggregates to form $2CaO \cdot SiO_2$. It was evident, however, that the reaction was still incomplete and that equilibrium had not been established.

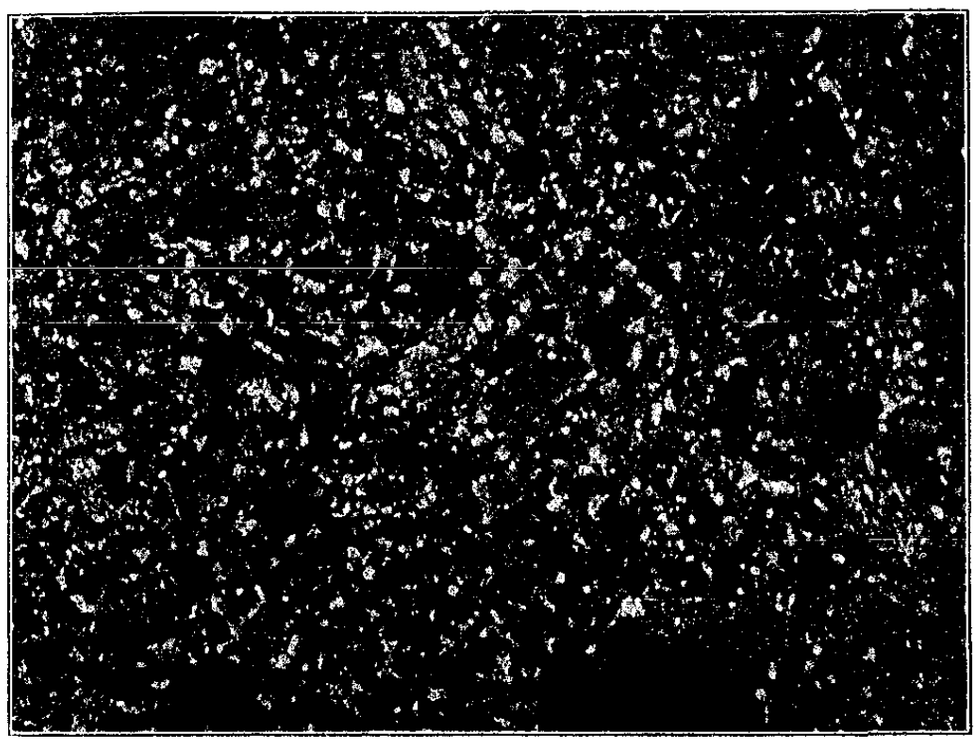


FIG. 4
Nicols crossed ×105
Photomicrograph of a thin section of charge 3, heated 30 hours at 1400°-1450°. Note the fine-grained structure with only an occasional large crystal.

(3) A charge of powdered drops was then heated to about 1600° for three hours, cooled to 1450° during one hour and held there at 1400°-1450° for thirty hours. This charge, Fig. 4, was evidently at or very close to equilibrium as only a very few fibrous aggregates were present and the section seemed to be made up of a nearly uniform mixture of grains of $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$ and $3CaO \cdot Al_2O_3$. The refractive indices of these compounds were measured on the powder by the immersion method to verify the observations made upon the thin section.

The above tests demonstrated clearly that these preparations were composed, at equilibrium, of the three compounds $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$ and $3CaO \cdot Al_2O_3$ instead of one ternary compound.

The possibility remained, however, that a ternary compound or solid solutions might exist in this region of the system at high temperatures and

decompose at lower temperatures giving at equilibrium the above mentioned compounds. If this were the case, X-ray studies might reveal the presence of such phases.

X-ray Studies[14]—In other studies in this laboratory pure $_3CaO \cdot SiO_2$, $_3CaO \cdot Al_2O_3$ and $\beta_2CaO \cdot SiO_2$ were prepared by burning the desired composition in a gas-fired or an electric furnace and regrinding and reburning



FIG. 5
Analyser out × 65
Composition $8CaO + Fe_2O_3 + 2SiO_2$. Note the fiber-like structure similar to that in Fig. 1.

until the product was homogeneous as shown by a microscopic examination. To obtain $\beta_2CaO \cdot SiO_2$ about one-half per cent of boric acid was added to the raw materials. A part of this is volatilized during the burning but that which remains is sufficient to prevent the beta to gamma inversion.

A mechanical mixture of the three compounds $_3CaO \cdot SiO_2$, $_3CaO \cdot Al_2O_3$ and $\beta_2CaO \cdot SiO_2$ was made up in equimolecular proportions which results in the composition $8CaO + Al_2O_3 + 2SiO_2$. The X-ray spectrum of this mixture was photographed on the same film as the spectrum of a powder made from the fused drops previously described. The spectrum of the latter preparation showed a few lines that the mechanical mixtures did not. These were found to be due to CaO[15].

In Table I are given the planar spacings and relative intensities of the lines found in the spectra of the $8CaO + Al_2O_3 + 2SiO_2$ preparation, of CaO and of the mixture of the three compounds, $_3CaO \cdot SiO_2$, $_2CaO \cdot SiO_2$, and $_3CaO \cdot Al_2O_3$.

[14] The X-ray data presented here were obtained by E. A. Harrington using the powder method devised independently by A. W. Hull: Phys. Rev., 10, 661 (1917), and by Debye and Scherrer: Physik. Z., 17, 277 (1916).

[15] CaO prepared from CaC_2O_4.

TABLE I

X-ray data obtained on the $8CaO + Al_2O_3 + SiO_2$ *preparations, mixtures of* $3CaO \cdot Al_2O_3$, $3CaO \cdot SiO_2$ *and* $2CaO \cdot SiO_2$, *and CaO.*

No. of line	Fused drops of composition $8CaO + Al_2O_3 + 2SiO_2$ Planar Spacings	Relative Intensity	Mixture of $3CaO \cdot SiO_2$ $2CaO \cdot SiO_2$, $3CaO \cdot Al_2O_3$ Planar Spacings	Relative Intensity	Calcium Oxide Planar Spacings	Relative Intensity	Compounds giving rise to the lines in the spectrum of the fused drops
1	3.03	4	3.03	4			$3CaO \cdot SiO_2$
2	2.77	10	2.77	10	2.77	7	CaO, $2CaO \cdot SiO_2$, $3CaO \cdot SiO_2$
3	2.69	10	2.69	10			$3CaO \cdot Al_2O_3$
4	2.60	4	2.60	4			$3CaO \cdot SiO_2$
5	2.39	5			2.40	10	CaO
6	2.27	.5	2.26	.5			$2CaO \cdot SiO_2$
7	2.18	7	2.18	8			$2CaO \cdot SiO_2$, $3CaO \cdot SiO_2$, $3CaO \cdot Al_2O_3$
8	2.03	1	2.04	1			$2CaO \cdot SiO_2$, $3CaO \cdot Al_2O_3$
9	1.975	2	1.970	2			$3CaO \cdot SiO_2$, $3CaO \cdot Al_2O_3$
10	1.895	7	1.895	7			$3CaO \cdot Al_2O_3$
11	1.755	4	1.758	5			$3CaO \cdot SiO_2$
12	1.695	4			1.700	10	CaO
13	1.627	5	1.630	3			$2CaO \cdot SiO_2$, $3CaO \cdot SiO_2$
14	1.550	8	1.552	8			$3CaO \cdot Al_2O_3$
15	1.483	4	1.485	3			$3CaO \cdot SiO_2$
16	1.450	2			1.450	8	CaO
17	1.385	1			1.388	8	CaO
18	1.345	3	1.342	2			$3CaO \cdot Al_2O_3$
19	1.200	4	1.202	4	1.201	6	CaO, $3CaO \cdot Al_2O_3$
20	1.095	2	1.093	1	1.101	6	CaO, $3CaO \cdot SiO_2$
21	1.076	.5			1.074	8	CaO
22	1.020	2	1.017	2			$3CaO \cdot Al_2O_3$
23	0.980	.5			0.979	7	CaO
24	0.900	1	0.896	1			$3CaO \cdot Al_2O_3$

The compounds causing each of the principal lines in the spectrum of the fused drops are listed in the last column of this table.

Since all lines in the spectrum of the fused preparation correspond to the lines in the spectra of the four compounds, and no shift in any of the lines or any appreciable change in the relative intensities could be detected, it seems to follow that no compounds other than those four are present and that no solid solution is present. The fibrous aggregates appear, therefore, to be one of these four compounds and their optical properties indicate that they are $_3CaO \cdot SiO_2$.

The form in which the $_3CaO \cdot SiO_2$ crystallizes from the drops seems to be dependent upon the conditions under which it is produced. In order to ascertain if it would be formed in the same way in other systems, the composition $8CaO + Fe_2O_3 + 2SiO_2$ was made up and drops prepared in the oxy-hydrogen flame. Fig. 5 shows a photomicrograph from a section of one of these drops. It may be observed that the same fiber-like crystals are obtained in this system. The birefraction and mean refractive index indicated also that they were $_3CaO \cdot SiO_2$. This constitutes further proof that the formation of fibrous aggregates is not dependent upon Al_2O_3 and, therefore, is not a ternary compound nor solid solution containing CaO, Al_2O_3 and SiO_2.

General Discussion

This investigation has been concerned with the study of a crystalline phase that appears to be different from any described by Rankin and Wright. This phase forms as fibrous aggregates when mixtures of the composition $8CaO + Al_2O_3 + 2SiO_2$ are heated at very high temperatures. The following points concerning this phase led one of us to believe that the ternary compound $8CaO \cdot Al_2O_3 \cdot 2SiO_2$ existed.

1. The abundance of the phase: some thin sections appeared to be composed almost entirely of these aggregates;

2. The form of the crystals: this appeared to be different from that of any of the equilibrium compounds;

3. The absence of predicted equilibrium compounds: the equilibrium to be expected according to the diagram of Rankin and Wright was not obtained when the preparations were heated for several days at 1200°.

By the experiments reported in this paper these aggregates have been broken up and preparations obtained which consisted of the three compounds $_3CaO \cdot SiO_2$, $_2CaO \cdot SiO_2$ and $_3CaO \cdot Al_2O_3$. This was made possible by furnaces which permitted the preparations to be heated for long periods at temperatures above 1400°. Such treatment was not possible with the furnace available for the study previously reported[7] and, therefore, the temperatures then used were not sufficient to establish equilibrium.

It has been shown by the experiments reported in this paper that these preparations, when at equilibrium, no longer contain the fibrous aggregates and that no one phase is present in such great proportions as were the aggregates in the original fused drops.

With respect to the abundance of the fiber-like phase, it is possible that several factors contributed to that appearance. Fig. 6 is a photomicrograph

under high magnification of a thin section of one of the original drops. There it may be seen that the fibrous crystals contain inclusions that could not be observed easily under lower magnifications. Likewise the X-ray method showed that the preparations contained $_2CaO \cdot SiO_2$ and $_3CaO \cdot Al_2O_3$ which could not be positively identified by the microscope.



FIG. 6
Nicols crossed, × 900
Photomicrograph of a thin section of the original drops. Note the minute inclusions in the aggregates.

Summary and Conclusions

An investigation has been made of the composition $8CaO + Al_2O_3 + {}_2SiO_2$ with the intention of studying the evidence bearing upon the existence of a compound of that composition.

By using the oxyhydrogen flame for preparing the samples, a crystalline phase was obtained which differed in appearance from the phases ordinarily found in mixtures of CaO, Al_2O_3 and SiO_2 heated to temperatures up to 1600°.

By proper heat treatments it was found possible to bring these preparations to the equilibrium found to exist in this system by Rankin and Wright.

The birefraction, mean refractive index and X-ray spectrum of this phase were the same as those obtained for $_3CaO \cdot SiO_2$.

The phase also forms in the composition $8CaO + Fe_2O_3 + {}_2SiO_2$ when treated in the same manner.

By use of high magnifications and the X-ray spectra of these preparations, they were shown to be inhomogeneous, containing other crystalline materials.

All of the evidence obtained in this study and presented here is opposed to the existence of a ternary compound of the composition $8CaO \cdot Al_2O_3 \cdot {}_2SiO_2$ stable in this system. This evidence likewise is opposed to the existence of solid solutions of the silicates and aluminates in this part of the system.

It is concluded that the fiber-like crystals previously reported by some as $8CaO \cdot Al_2O_3 \cdot {}_2SiO_2$ are $_3CaO \cdot SiO_2$.

U. S. Bureau of Standards,
July 7, 1926.

AQUEOUS SOLUTIONS OF SODIUM SILICATES.
VII. SILICATE IONS.
ELECTROMETRIC TITRATIONS: DIFFUSION: COLORIMETRIC ESTIMATION.

BY R. W. HARMAN

Introduction

From the papers already communicated by the author on the subject of aqueous solutions of varying ratio $Na_2O:SiO_2$, it is seen that the existence of definite silicate ions in these solutions rests on three main sources of evidence, viz.

(1) Conductivity measurements[1] resulted in the finding of a much greater conductivity for ratios up to 1:2 than could result alone from such a proportion of NaOH formed by hydrolysis as measured by the E.M.F. method. Above ratio 1:2, where the OH ion concentration is very low, the sodium ion accounts for only about one-half the conductivity found. The only way to account for the conductivity is to postulate the existence of silicate ions with mobilities ranging from 40-60 approximately. Moreover, the equivalent conductivity calculated from the concentration of sodium, hydroxyl and silicate ions, as found from F. Pts., OH and Na ion measurements, and their respective mobilities, agree well with the experimentally determined conductivity results.

(2) The most direct and conclusive evidence so far put forward to show that the silica in aqueous solutions of these ratios carries an electric charge is obtained from the results of transport number experiments.[2] There it was shown by the author that $V_{II_{S_i}}$ is 0.16 for ratio 1:1, 0.41 for ratio 1:2, 0.46 for 1:3 and 0.59 for 1:4, when calculated on the basis that the T. N. of the silicate is given by

$$\text{T.N. silicate} = \frac{\text{total change in weight of } SiO_2}{N \times (\text{wt. of } SiO_2 \text{ equivalent to Ag deposited in coulometer})}$$

where N = ratio. Whether this basis of calculation is correct or not these transport number experiments prove that quite a fair proportion of the current, at least one-half in the higher ratios, is carried by the silica. Since the possibility of adsorbed OH ions on the silica giving the necessary charge to the silica, has been shown to be remote and indeed most improbable[3], the only conclusion is that the silica must exist as ions. The relatively high mobility of these charged silica particles as deduced from conductivity and transport number results, is also contrary to that expected from colloidal aggregates with OH ions adsorbed thereon.

[1] Harman: J. Phys. Chem., **29**, 1155 (1925).
[2] Harman: J. Phys. Chem., **30**, 359 (1926).
[3] Harman: J. Phys. Chem., **31**, 355 (1927).

(3) A third very weighty argument appears when we consider the result of hydrolysis experiments along with freezing point lowering results. In the paper on osmotic activity[1] it was shown that the only possible way to account for the high osmotic activity of these ratios in aqueous solution was to accept the existence of silicate ions. The conductivity of the sodium ions and of the hydroxyl ions as found by E.M.F. experiments of Na ion and OH ion activities, together account for only a fraction of the total ion concentration as determined by vapour pressure and freezing point lowering. The non-accordance is quite beyond the bounds of experimental error, nor could it be accounted for by the assumptions underlying the laws governing ideal solutions. The higher the ratio the wider the divergence, so that in 1:3 and 1:4 more than half the crystalloidal content has to be accounted for by the silica in the most dilute solutions. Whether this is due to the complex silica aggregate breaking down into simpler silicate ions, or to the disintegration of an ionic micelle, or to crystalloidal H_2SiO_3 ionising, or to all these phenomena, can not be discussed fully at present. The fact remains however, of the existence of a very large proportion of "crystalloidal" silica in solution.

The existence of crystalloidal silica and silicate ions in aqueous solutions seems therefore firmly established, and there now remains the problem of the nature and composition of the ions and the proportions in which they exist. In the solution of this problem the nature and composition of the salts giving rise to these ions furnish a good guide, and help to narrow down the possibilities.

From the investigation of the ternary system[2] $Na_2O : SiO_2 : H_2O$ at 25°C we have seen that the ratios 1:1 and 1:2 only are definite salts. Ratio 1:1 is the metasilicate, Na_2SiO_3, crystallising with 9, 6, and 2.5 aq., the existence of which has been long established in spite of the difficulty of its crystallisation and the confusion which till now has existed concerning its hydrates.

A certain amount of evidence that these two ratios 1:1 and 1:2 are definite salts is also forthcoming from consideration of the curves where conductivity, hydroxyl ion concentration, sodium ion concentration, and the van't Hoff factor "i" from freezing points are severally plotted against the ratio, distinct changes of direction at these points being evident. It was also seen from consideration of freezing point results[3] that the existence of salts corresponding to ratios 1:3 and 1:4 was very unlikely. From the diagram of the ternary system $Na_2O : SiO_2 : H_2O$ (loc. cit.) the fact that the solubility of the definite salt 1:2 extends to the region 1:3 and 1:4 seems to indicate also that salts corresponding to 1:3 and 1:4 are unlikely. Ratio 1:2 may be either a salt of the formula $NaHSiO_3$ or $Na_2Si_2O_5$. It is not proposed to give here all the evidence for and against these two salts, except to state that (1) Morey[4] has obtained $Na_2Si_2O_5$ from melts at high temperatures over 400°C but not from solutions at ordinary temperatures (2) the only one authentic case of a

[1] Harman: J. Phys. Chem., **31**, 355 (1927).
[2] Harman: J. Phys. Chem., **31**, 511 (1927).
[3] Harman: J. Phys. Chem., **31**, 511 (1927).
[4] Morey: J. Phys. Chem., **28**, 1167 (1924).

disilicate occurring naturally is *rivaite*[1], and that in small amounts from Vesuvius (3) the author's results on freezing point lowering (loc. cit.) would seem to indicate $NaHSiO_3$.

With the object of obtaining more experimental data on the subject and of attempting to obtain further insight into the constitution and concentration of crystalloidal silica, of silicic acid or acids and of silicate ions, experimental word was commenced on electrometric titrations, and on diffusion and on colorimetric determination of the silicate ion. Although only a few results have so far been obtained, their nature is sufficiently important to warrant publication at this stage.

The silicates used, their preparation nomenclature etc. are the same as described in previous communications on this subject by the author.

Electrometric Titrations and Dissociation Constants of H_2SiO_3

While attempting to calculate the dissociation constants of H_2SiO_3 from hydrolysis data it was thought that electrometric titrations would probably afford a more direct and accurate method of calculation. Only a few experiments have so far been carried out, and, while admitting that this section of the work is far from complete, it is thought that the results are sufficiently instructive and interesting to be included here.

Experimental

A dilute solution of ratio 1:1 was put in the hydrogen electrode vessel; hydrogen was bubbled through until the E.M.F. became steady; then small, measured quantities of standardised HCl solution were run in from a burette, and the E.M.F. noted after each addition of HCl. The hydrogen was kept bubbling through the electrode vessel during the whole experiment.

Results

Two such experiments only, have so far been carried out,—

(1) 0.1 N. HCl added to 0.1 N. Na_2SiO_3.

(2) 1.219 N. HCl added to 0.2 N. Na_2SiO_3.

In both, when the E.M.F. observed is plotted against the amount of HCl added as in Fig. 1, there is a small unmistakable drop of E.M.F. in the neighbourhood of 0.9250 volts, i.e. at point B in the figure, followed by a large and sudden drop from 0.8000 volts to 0.4000 volts.

The mid-point A of the large drop comes at 0.6005 volts with 0.1 N. Na_2SiO_3, and at 0.6000 volts with 0.2 N. Na_2SiO_3. The neutral point of water is at 0.7000 volts. (N. KCl calomel cell used).

The amount of HCl added, corresponding to point A, is equal to the calculated amount just sufficient to neutralize all the sodium in solution, while the amount of HCl added is, in both cases, at the mid-point B of the smaller drop, about one-half that corresponding to point A. This is good evidence of the existence of the acid metasilicate $NaHSiO_3$.

From these two curves we conclude that H_2SiO_3 ionises in two stages,—

(1) $H_2SiO_3 \rightleftarrows H^{\cdot} + HSiO_3' \ldots\ldots (k_1)$.

(2) $HSiO_3' \rightleftarrows H^{\cdot} + SiO_3'' \ldots\ldots (k_2)$.

[1] Zambonini: Atti. Accad. Sci. Nap., **12**, No. 12, p. 16 (1912).

Point B corresponds to equation (2), and at that point the following equilibrium exists,—

$$Na_2SiO_3 + HCl \rightleftarrows NaHSiO_3 + NaCl.$$

Point A corresponds to equation (1) and at that point the main equilibrium is

$$NaHSiO_3 + HCl \rightleftarrows H_2SiO_3 + NaCl.$$

If the fall in E.M.F. at point B had been more definite, i.e. larger and sharper, then it would have been possible to calculate k_2, the second dissociation constant of H_2SiO_3 therefrom with accuracy; as it is, it has been considered more prudent to omit assigning any definite value to k_2 until further work has been done with this specific point in view.

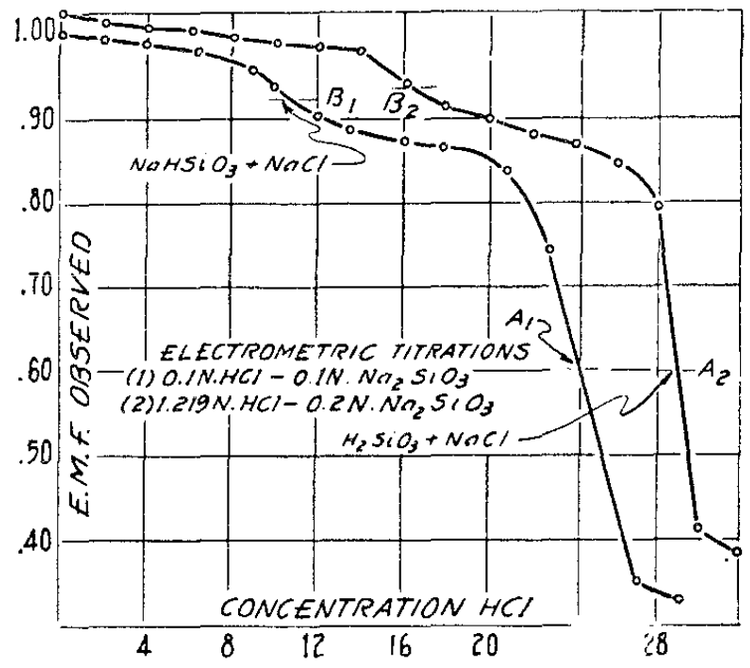


FIG. 1

First Dissociation Constant k_1

$$H_2SiO_3 \rightleftarrows H^{\cdot} + HSiO_3'$$

Point A_2, E.M.F. = 0.6000 volts (Fig. 1, curve 2.).
Conc. Na_2SiO_3 = 0.1 molar.
pH = 5.33. $[H^{\cdot}] = 0.47 \times 10^{-5}$. $[HSiO_3'] = 0.47 \times 10^{-5}$.
$[H_2SiO_3]$ equals 0.1 m nearly; assuming, for which there is good reason given later, that the H_2SiO_3 is not colloidal,
Then,—

$$[H^{\cdot}] \times [HSiO_3'] = k_1 . [H_2SiO_3]$$

$$\therefore k_1 = \frac{(0.47 \times 10^{-5})^2}{0.1}$$

$$= 2.2 \times 10^{-10}.$$

For curve (1), Fig. 1, conc. Na_2SiO_3 equals 0.05m, and E.M.F. = 0.6005 volts, i.e. $[H^{\cdot}] = 0.46 \times 10^{-5}$, hence, $k_1 = 4.2 \times 10^{-10}$.

An attempt was also made to titrate electrometrically NaOH and silicic acid, but here it is not of much use to begin with silicic acid or so-called

silicic acid prepared by dialysis, as this must necessarily be almost completely colloidal.

Instead, a dilute solution, 0.2 N_w, of one of the ratios rich in silica, viz. 1:4, was taken and 10 N. NaOH added, the E.M.F. being measured after successive additions of measured quantities of NaOH, (the NaOH being added in drops.).

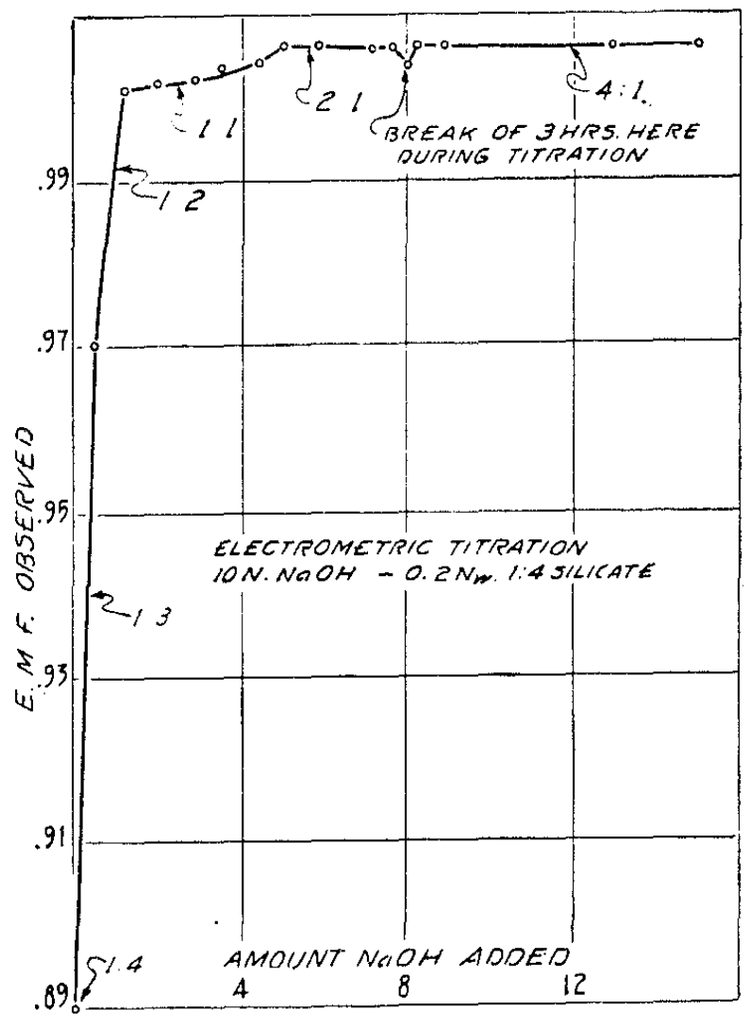


FIG. 2

The result is shown graphically in Fig. 2 where the E.M.F. observed is plotted against the quantity of NaOH added. This curve is different from that of OH ion concentration against ratio,[1] because there the sodium was kept constant while here the SiO_2 is being kept constant.

We note that the E.M.F. rises very rapidly until just beyond ratio 1:2, but only slightly and irregularly after that, until at 2:1 a fairly constant value is obtained.

It is doubtful however, whether the mixture reaches equilibrium in so short a time, and during the titration a break of three hours was made. At the end of this three hours, the E.M.F. had fallen until the value was almost

[1] Harman: J. Phys. Chem., **30**, 1100 (1926). Fig. 2.

the same as at 1:1. This is indicated at point X on the figure. On further addition of NaOH the E.M.F. again increased to a constant value.

We cannot conclude much from this one curve alone, except that,—

(1) the mixture of silicate and NaOH does not reach equilibrium immediately, a conclusion already arrived at from conductivity measurements.

(2) the OH ion concentration of ratio 2:1 is not much greater than that of 1:1; this has already been noticed in the paper on hydrolysis.

Calculation of Dissociation Constants of H_2SiO_3 from Hydrolysis Data

One would expect metasilicic acid, H_2SiO_3, the dibasic acid which forms the metasilicate $NaSiO_3$, to ionise in two stages, and indeed there is evidence of its so doing from the electrometric titrations of Na_2SiO_3 against HCl just described.

Considering the hydrolysis of Na_2SiO_3 in two stages we can calculate the primary and secondary dissociation constants of H_2SiO_3 in the following manner.

Secondary Dissociation Constant k_2

$$\underset{\substack{(1-x)\\ \alpha_1}}{Na_2SiO_3} + H_2O \rightleftarrows \underset{\substack{x\\ \alpha_2}}{NaHSiO_3} + \underset{\substack{x\\ \alpha_3}}{NaOH} \qquad (1)$$

where x = fraction hydrolysed, and α_1, α_2 and α_3 the respective degrees of ionisation. If we put $\alpha_2 = \alpha_3 = 1$, i.e. NaOH and $NaHSiO_3$ completely dissociated, and take the values given for OH and Na ion concentrations from the E.M.F. measurements already communicated for x and α_1 respectively we get,—

$$k_2 = \frac{[H^{\cdot}] \times [SiO_3'']}{[HSiO_3']}$$

Hence,—

$$\frac{K_w}{k_2} = \frac{x^2}{(1-x)c} - \frac{\alpha_2^2.}{\alpha_1}$$

N_w	conc. m	x	α_1	K_w/k_2	k_2
0.1	0.05	0.414	0.03	195.0	0.51×10^{-16}
0.05	0.025	0.440	0.11	125.7	0.80
0.02	0.01	0.465	0.75	53.89	1.86
0.01	0.005	0.556	0.10	139.3	0.7
				Mean =	0.97×10^{-16}.

Product of Dissociation Constants, $k_1.k_2$.

Considering the second stage,—

$$NaHSiO_3 + H_2O \rightleftarrows NaOH + H_2SiO_3 \qquad (2)$$

we get,—

$$k_1 = \frac{[H^{\cdot}] \times [HSiO_3']}{[H_2SiO_3]}$$

Combining equations (1) and (2),—

$$Na_2SiO_3 + 2\,H_2O \rightleftarrows H_2SiO_3 + 2\,NaOH$$
$$[H^{\cdot}]^2 \times [SiO_3''] = k_1.k_2\,[H_2SiO_3].$$

Hence

$$\left(\frac{K_w}{2\alpha_2 xc}\right)^2 . \alpha_1\,(1-x)c = k_1.k_2.xc.$$

For conc. C = 0.05m, we get $k_1.k_2 = 8.3 \times 10^{-25}$.

Hence $k_1 = k_1.k_2 / k_2$
$= 1.6 \times 10^{-10}$.

Comparison of Dissociation Constants of H_2SiO_3

	From electrometric titration	From hydrolysis
$k_1 . k_2$		8.3×10^{-25}
k_1	4.2×10^{-10}	1.6×10^{-10}
k_2		0.51×10^{-16}

Silicate Ions

Hitherto the silica in solution has usually been regarded as wholly colloidal in nature, whether a solution of an alkali silicate or of silicic acid has been the subject of investigation. In view of the fact that the present investigations indicate that in some cases the silica is almost wholly crystalloidal, it seemed most advisable to obtain some direct evidence of the presence of silicate ions. This has been done in two ways,—

(1) colorimetrically.
(2) by diffusion.

Colorimetric Estimation of Silica

Diénert and Waldenbulcke[1] describe a colorimetric test for crystalloidal silica depending on the formation of a greenish yellow silicomolybdate.

On adding 2 cc. of a 10% solution of ammonium molybdate and 4 or 5 drops of a 50% solution of H_2SO_4 to a silicate solution, a yellow colour forms immediately in the cold, which deepens for 10 minutes or so and then remains constant for several hours. The test is perfectly quantitative in dilute solution.

The mechanism of the reaction involved does not seem to be very clearly understood as yet. W. Asch[2] has shown the existence of the two salts,— $2Na_2O.SiO_2.12MoO_3.aq.$ and $1.5Na_2O.0.5H_2O.SiO_2.12MoO_3.aq.$, and that in these salts the silicic and molybdic acids form a complex ion.

Many compounds of silica besides the simple silicates investigated here, e.g. K_2SiF_6, give the test, but colloidal silicic acid, i.e. silicic acid prepared by lengthy diffusion does not give any colour, so that at best this colorimetric test can only be said to be a test for crystalloidal silica and not a test for any particular silicate ion, although probably the ion concerned is the simple silicate SiO_3 ion from metasilicic acid.

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[1] Compt. rend., **176**, 1478 (1923).
[2] "The Silicates in Chemistry and Commerce", 16 (1923).

The following Table I contains the results of this colorimetric test on ratios 2:1, 1:3 and 1:4. Ratio 1:1 was used as a standard, and the table shows the normality in terms of sodium content of ratio 1:1 required to give the same depth of colour as the normality cited for the other ratios, and the ratio of crystalloidal silica in 2:1, 1:3 and 1:4 to the crystalloidal silica in 1:1.

TABLE I

2:1	Std. 1:1	Crys. sil. in 2:1 / Crys. sil. in 1:1	1:3	Std. 1:1	1:3 / 1:1	1:4	Std. 1:1	1:4 / 1:1
0.0005	0.00025	0.5	0.0005	0.0015	3.0	0.0005	0.0002	4.0
0.001	0.0005	0.5	0.001	0.0025	2.8	0.001	0.004	4.0
0.002	0.001	0.5	0.003	0.009	3.0	0.003	0.010	3.3
0.003	0.0015	0.5	0.005	0.014	2.8	0.005	0.016	3.2
0.004	0.002	0.5	0.007	0.018	2.6	0.007	0.022	3.1

It is seen that in very dilute solution, 0.005 N, ratio 1:4, contains as much crystalloidal silica as 0.002 N, 1:1, the normalities in accordance with the practice adopted in this investigation being expressed in terms of the sodium content. In other words, practically all the silica in ratio 1:4 exists in the crystalloidal state at a dilution of 0.005 N, or more correctly, ratio 1:4 contains 4 times as much crystalloidal silica as ratio 1:1 at this dilution.

Similarly at this dilution, all the silica in ratios 2:1 and 1:3 exist in the crystalloidal state.

As the solution gets more concentrated we see that ratio 1:4 no longer contains 4 times as much crystalloidal silica as ratio 1:1, indicating that in the more concentrated solutions some of the silica in ratio 1:3, and still more in ratio 1:4, passes into the colloidal state.

Hence in extremely dilute solutions of these ratios practically all the silica exists in the crystalloidal state, but with increasing concentration increasing amounts of colloidal silica are manifested.

Diffusion Experiments

The diffusion experiments were carried out with collodion membranes and with parchment paper. The collodion membranes were prepared in the form of a flask and were closed by a rubber stopper, through which a glass tube serving as a manometer passed, the whole being made airtight by coating the neck of the bag and the stopper with collodion.

It was found that all the ratios at all concentrations gave evidence of diffusion of silicate ions both with the collodion membrane and with parchment paper.

Diffusion was allowed to proceed for from 8-14 days (equilibrium being usually established in 6 or 7 days) and then the solutions inside and outside the membrane were analysed.

Results

With ratios 1:1 and 1:2 equal distribution of both sodium and silica was found to have taken place with a 0.3 N_w solution.

In ratio 1:3, with a solution approximately 0.2 N_w, after equilibrium had been established in a couple of days, there was an excess of silica within the membrane, thus showing that some of the silica in the original solution was colloidal.

More definite evidence of the existence of the silica as partly colloidal, partly crystalloidal, was obtained with a 0.3 N_w solution of ratio 1:4. The sodium content of the inside and the outside solutions was practically the same after 12 days diffusion, but there was 3.567% SiO_2 outside and 4.967% SiO_2 inside the membrane. Assuming the difference to be colloidal silica, i.e. non-diffusible silica, then in the original solution 1.4/4.2 = 1/3 of its silica, was in the colloidal state.

It is not surprising that the general belief exists that silicic acid is almost wholly colloidal in solution when it is remembered, that it is prepared by dialysis, during which the crystalloidal constituent diffuses through the membrane and is discarded, leaving only the colloidal part. Any investigation into the nature of silicic acid should not, as has hitherto been the case, be confined to this colloidal proportion alone.

It was found that when a 1 N_w solution of ratio 1:1, to which a small excess of HCl had been added, was submitted to dialysis, silica rapidly diffused through the membrane, as much as 30% of the original SiO_2 content being diffusible.

Although this was observed and pointed out by Graham in his classic researches, its significance does not seem to have been generally recognised. When the outside water is changed continually, as in ordinary dialysis, a solution of silicic acid remained, which gave only the very slightest colour with ammonium molybdate and thus was practically all colloidal.

Conclusion

It has thus been shown conclusively that silicate ions exist in all the ratios up to 1:4, and in silicic acid itself. In 1:1 and 1:2 the silica is practically all crystalloidal in dilute solution, in ratios 1:3 and 1:4 increasing proportions are colloidal, and in extremely dilute solution, practically all the silica in any of these ratios here investigated exists in the crystalloidal state.

Summary

(1) Electrometric titrations of 0.1 and 0.2 N_w . Na_2SiO_3 with 0.1 N and 1.219 N . HCl, and 0.2 N_w . Na_2SiO_3, 1:4, with 10 N . NaOH have been carried out.

(2) The curves obtained with Na_2SiO_3 and HCl are typical of dibasic acids, thus suggesting H_2SiO_3 as dibasic with salts $NaHSiO_3$ and Na_2SiO_3.

(3) The primary and secondary dissociation constants have been calculated from hydrolysis results and from these electrometric titrations; $k_1 = 4.2 \times 10^{-10}$ and $k_2 = 0.51 \times 10^{-16}$.

(4) The amount of crystalloidal silica in ratios 2:1, 1:3 and 1:4 has been compared with that in ratio 1:1 in very dilute solution by means of the colorimetric test with H_2SO_4 and ammonium molybdate.

(5) In very dilute solution most of the silica in these ratios is crystalloidal, but increase of concentration and increase of ratio increase the colloidal content.

(6) Diffusion experiments through membranes of collodion and parchment paper indicate that most of the silica in ratios 1:1 and 1:2 is diffusible; about 2/3 of the silica in 0.3 N_w 1:4, and about 1/3 in 1.0 N_w H_2SiO_3 was crystalloidal.

(7) H_2SiO_3 is much stronger than hitherto supposed, due no doubt to the fact that when prepared by continuous dialysis the ionisable and diffusible portion is lost.

I wish to thank the Commissioners of the 1851 Exhibition for a Scholarship which has enabled me to carry out this investigation, and to express my gratitude to Professor Donnan at whose suggestion this work was undertaken, for his constant kindly interest and advice.

The Sir William Ramsay Laboratories of Physical and Inorganic Chemistry,
University College, London.
October 14, 1926.

STUDIES ON THE TRANSFORMATIONS OF IRON IN NATURE
I. THEORETICAL CONSIDERATIONS

BY H. O. HALVORSON AND R. L. STARKEY*

Ever since man began to study nature his attention has been attracted by the transformations that take place. Since the transformations that attract the most attention are generally those that are accompanied by visible modifications, some of the changes of iron are particularly striking since here they are accompanied by the precipitation of the red oxides that are so plainly visible. These changes are interesting not only from a purely scientific standpoint but are of great economic importance, since they are responsible for the deposition of many formations of iron ore and are also concerned in the corrosion of iron, which in itself is of great economic importance.

Due to the great importance of these reactions, men from many different fields with widely different viewpoints have attempted to explain the agencies responsible for them. From these studies there have been developed various theories some of which definitely conflict. The pure chemist with slight appreciation of biology has presented explanations assuming no activity of biological agencies. On the other hand biologists have often attempted to explain the transformations with little regard for the chemical laws that must be obeyed even in biological processes. It is the object of these studies to indicate some of the fundamental chemical reactions governing the changes and the importance of some organisms in determining the courses of these reactions by their effects in modifying the physical environment. The fundamental equations developed in this paper shall be used in other papers to interpret the mechanism of the transformations.

It will simplify matters to consider first the equilibrium conditions that must be fulfilled in an inorganic solution containing iron in which no complex ions of iron are formed. In the following equilibrium conditions it is assumed therefore that no complex ions are formed. From the deductions arrived at by such a consideration it will be possible to predict in a qualitative way what influence the formation of complex ions will have upon the system. In a solution containing ferrous ions the oxygen of the air will oxidize some of these ions to the ferric form. This change can be indicated by the following reaction:

$$4\,Fe^{\cdot\cdot} + O_2 + 2\,H^{\cdot} \rightleftarrows 4\,Fe^{\cdot\cdot\cdot} + 2\,OH' \qquad (1)$$

From the law of mass action we know that the equilibrium state will be expressed by the following equation:

$$\frac{[A_{Fe^{\cdot\cdot}}]^4\,[A_{O_2}]\,[A_{H^{\cdot}}]^2}{[A_{Fe^{\cdot\cdot\cdot}}]^4\,[A_{OH'}]^2} = K \qquad (2)$$

*Department of Bacteriology and Immunology, University of Minnesota.

In this equation $A_{Fe^{\cdot\cdot}}$ is the activity of the ferrous ions expressed in moles per liter, A_{O_2} the activity of the dissolved oxygen, $A_{H^{\cdot}}$ the activity of the hydrogen ions, etc. K is the equilibrium constant.

From the dissociation of water we can get the following equilibrium equation:

$$[A_{H^{\cdot}}]\ [A_{OH'}] = K_W \tag{3}$$

Combining (2) and (3) we get:

$$\frac{[A_{Fe^{\cdot\cdot}}]^4\ [A_{O_2}]\ [A_{H^{\cdot}}]^4}{[A_{Fe^{\cdot\cdot\cdot}}]^4} = K(K_w)^2$$

This can be rearranged as follows:

$$\frac{[A_{Fe^{\cdot\cdot}}]}{[A_{Fe^{\cdot\cdot\cdot}}]} \cdot [A_{H^{\cdot}}] = \frac{K}{[A_{O_2}]^{\frac{1}{4}}} \tag{4}$$

If the solution is saturated with respect to ferric hydroxide the following equation will hold.

$$[A_{Fe^{\cdot\cdot\cdot}}]\ [A_{OH'}]^3 = K_i \tag{5}$$

(6) From (3) and (5)
$$\frac{[A_{Fe^{\cdot\cdot\cdot}}]}{[A_{H^{\cdot}}]^3} = K''$$

(7) From (4) and (6)
$$\frac{[A_{Fe^{\cdot\cdot}}]}{[A_{H^{\cdot}}]^2} = \frac{K'''}{[A_{O_2}]^{\frac{1}{4}}}$$

If the pressure of the oxygen is kept constant, then

$$\frac{[A_{Fe^{\cdot\cdot}}]}{[A_{H^{\cdot}}]^2} = C. \tag{8}$$

From the hydrolysis of ferrous ions we have the following reaction taking place:

$$Fe^{\cdot\cdot} + 2\ HOH \rightleftarrows Fe(OH)_2 + 2\ H^{\cdot}$$

The equilibrium equation will be

$$\frac{[A_{Fe^{\cdot\cdot}}]}{[A_{H^{\cdot}}]^2} = K_n\ [A_{Fe(OH)_2}] \tag{9}$$

(10) From (8) and (9) $K_n\ [A_{Fe(OH)_2}] = C$

It is evident from this that in a solution of ferrous iron in contact with atmospheric pressure of oxygen and solid ferric hydroxide the activity of the un-ionized ferrous hydroxide is fixed. This activity is independent of the pH but varies only with the oxygen pressure. This will be equivalent to the establishment of a solubility product for ferrous hydroxide even though the solution is not in equilibrium with the solid ferrous hydroxide. This will make it rather convenient to calculate the amount of ferrous iron that can remain in a solution at any pH.

The constant expressed in equation (9) above can be evaluated with sufficient accuracy for this theoretical consideration without much difficulty. In a dilute solution the concentration can be put equal to the activity without introducing much error. In a dilute solution of ferrous sulphate which has come to equilibrium the concentration of the ferrous ions can be put equal to

the total amount of iron in solution with no appreciable error. For the evaluation of the above-mentioned constant a series of solutions of ferrous sulphate were made up and allowed to come to equilibrium by standing open to the atmosphere for a period of four months. At the end of this time pH determinations were made of the solutions after which they were analyzed for total iron in solution. In order to determine the concentration of the iron, a sample of 2500 cc. was evaporated to dryness and the residue dissolved in a total volume of 50 cc. Two 20 cc. samples of this were taken and analyzed for iron by the oxidation with potassium dichromate, using the ferricyanide test for the end point. The pH was determined with a Leeds and Northrup Type K potentiometer, using a N/1 calomel half-cell as a standard electrode and a Bailey electrode for the hydrogen electrode. The results are given in Table I.

TABLE I

Conditions existing in solutions of ferrous sulphate in contact with air and in equilibrium with solid ferric hydroxide

Per cent $FeSO_4$ in original solution. Approximate	pH	Moles of iron per liter. Final	Log Fe	Log $\frac{Fe}{[A_{H\cdot}]^2}$	$\frac{Fe}{[A_{H\cdot}]^2}$
.002	4.228	.0000188	5.274-10	3.730	5.38×10^3
.002	4.471	.00000672	4.827-10	3.769	5.88×10^3
.002	4.307	.0000134	5.128-10	3.742	5.52×10^3
.005	3.789	.000106	6.027-10	3.605	4.03×10^3
.005	3.893	.0000984	5.993-10	3.779	6.02×10^3
.005	3.787	.0001000	5.999-10	3.573	3.74×10^3
.008	3.677	.000180	6.261-10	3.653	4.50×10^3
.008	3.669	.000190	6.279-10	3.606	4.04×10^3
.008	3.677	.000180	6.261-10	3.653	4.50×10^3
.01	3.645	.000240	6.380-10	3.670	4.68×10^3
.01	3.623	.000242	6.383-10	3.629	4.26×10^3
				Average	4.77×10^3

If we assume that these solutions are sufficiently dilute to put the concentration of the iron as determined by titration to be equal to the activity, we can average the values obtained in the last column and we get

$$\frac{[A_{Fe^{\cdot\cdot}}]}{[A_{H\cdot}]^2} = 4.8 \times 10^3.$$

The above assumption will introduce a slight error but the value is sufficiently accurate for this consideration. Experiments are now in progress in which the constant can be evaluated without this assumption. This will be published at a later date.

The concentrations of iron occurring in nature where precipitation of ferric iron is noted are extremely low. These solutions will be so dilute that not much error will be made by assuming that the concentration of ferrous iron is equal to the activity. The ratio of the activity of the ferrous ion over

the square of the activity of the hydrogen ion, which is approximately equal to 4.8×10^3, will be used to interpret the mechanism of iron precipitation.

From this ratio it is possible to indicate what amount of iron can remain in solution at various hydrogen ion concentrations where no complex ions are formed. This is illustrated in Table II.

TABLE II

Ferrous ions held in solution at various pH values

pH	$[A_{H^\cdot}]^2$	$A_{Fe^{\cdot\cdot}}$	Parts of $Fe^{\cdot\cdot}$ per M.
3.0	$1. \times 10^{-5}$	4.8×10^{-3}	270.
4.0	$1. \times 10^{-8}$	4.8×10^{-5}	2.70
5.0	$1. \times 10^{-10}$	4.8×10^{-7}	.027
6.0	$1. \times 10^{-12}$	4.8×10^{-9}	.00027
7.0	$1. \times 10^{-14}$	4.8×10^{-11}	.0000027

In the last column are given the parts of ferrous iron that can remain in solution in a million parts of the solvent. The values given for pH of 3 and 4 are probably much too low since the activities here may be less than the concentration. By considering Table II and equation (1) above it can be seen that as the pH of the water is changed from 4 to 5 the ferrous iron will precipitate as ferric hydroxide. It also shows what the pH of the medium must be in order to hold any amount of iron in solution under atmospheric conditions.

From equation (4) when the pressure of the oxygen is kept constant we know that

$$\frac{[A_{Fe^{\cdot\cdot}}]}{[A_{Fe^{\cdot\cdot\cdot}}]} \cdot [A_{H^\cdot}] = K.$$

This constant can now be evaluated for the equilibrium condition under atmospheric conditions. We already have

$$\frac{[A_{Fe^{\cdot\cdot}}]}{[A_{H^\cdot}]^2} = 4.8 \times 10^3 \tag{11}$$

The solubility product of ferric hydroxide has been determined with some degree of accuracy and is given in the literature[1] as follows:

$$[A_{Fe^{\cdot\cdot\cdot}}]\ [A_{OH'}]^3 = 1.1 \times 10^{-36}$$

From this and the dissociation product of water the product becomes:

$$\frac{[A_{Fe^{\cdot\cdot\cdot}}]}{[A_{H^\cdot}]^3} = \frac{1.1 \times 10^{-36}}{1 \times 10^{-42}} = 1.1 \times 10^6 \tag{12}$$

Dividing (11) by (12) we get:

$$\frac{[A_{Fe^{\cdot\cdot}}]}{[A_{H^\cdot}]^2} \cdot \frac{[A_{H^\cdot}]^3}{[A_{Fe^{\cdot\cdot\cdot}}]} = \frac{4.8 \times 10^3}{1.1 \times 10^6} = 4.4 \times 10^{-3}$$

or

$$\frac{[A_{Fe^{\cdot\cdot}}]}{[A_{Fe^{\cdot\cdot\cdot}}]}[A_{H^\cdot}] = 4.4 \times 10^{-3}$$

From this equation it is possible to calculate at different pH values what

[1] Cited from E. Müller in Landolt-Börnstein: "Physikalisch-Chemische Tabellen." 4th Ed. p. 1201 (1912).

the stable ratio of $\frac{[A_{Fe^{\cdot\cdot}}]}{[A_{Fe^{\cdot\cdot\cdot}}]}$ will be. Knowing the value for this ratio and the value of $[A_{Fe^{\cdot\cdot}}]$ as indicated in Table II, it is possible to evaluate $[A_{Fe^{\cdot\cdot\cdot}}]$ for different pH values. This is shown in Table III.

TABLE III

Amounts of ferric iron held in solution at different pH values

pH	$[A_{H^{\cdot}}]$	$\frac{[A_{Fe^{\cdot\cdot}}]}{[A_{Fe^{\cdot\cdot\cdot}}]}$	Parts of $Fe^{\cdot\cdot\cdot}$ per M.
3.0	1×10^{-3}	4.4×10^{0}	6.1×10^{1}
4.0	1×10^{-4}	4.4×10^{1}	6.1×10^{-2}
5.0	1×10^{-5}	4.4×10^{2}	6.1×10^{-5}
6.0	1×10^{-7}	4.4×10^{3}	6.1×10^{-8}
7.0	1×10^{-6}	4.4×10^{4}	6.1×10^{-11}

It is evident from this table that in solutions having pH values of 4 or above that the total iron in the solution is practically equal to the ferrous iron in solution. As the solution becomes more basic the ratio of ferrous to ferric becomes greater.

The above deductions are made on the condition that the solution be in equilibrium with solid ferric hydroxide and be in equilibrium with atmospheric oxygen. It may be of interest to inquire into the state of affairs if the oxygen pressure is varied. Some light may be thrown on this by considering the original oxidation equation.

$$4\ Fe^{\cdot\cdot} + O_2 + 2\ H^{\cdot} \rightleftarrows 4\ Fe^{\cdot\cdot\cdot} + 2\ OH'$$

If this is a reversible reaction we can drive the reaction in either direction by varying the activity of the oxygen. The equilibrium equation is as follows:

$$\frac{[A_{Fe^{\cdot\cdot}}]}{[A_{Fe^{\cdot\cdot\cdot}}]} \cdot [A_{H^{\cdot}}] = \frac{K}{[A_{O_2}]^{\frac{1}{4}}}$$

If we assume that the activity of the oxygen is unity at atmospheric pressure, we can say that where $[A_{O_2}] = 1$ then $K = 4.4 \times 10^{-3}$ and $\frac{[A_{Fe^{\cdot\cdot}}]}{[A_{Fe^{\cdot\cdot\cdot}}]} \cdot [A_{H^{\cdot}}] = \frac{4.4 \times 10^{-3}}{[A_{O_2}]_P^{\frac{1}{4}}}$ where $[A_{O_2}]_P$ represents the difference between the activity of the oxygen at pressure p and at atmospheric pressure. In general the activity of the oxygen will vary directly as the pressure. By fixing our conditions so that the pressure of the oxygen is low, at equilibrium

$$\frac{[A_{Fe^{\cdot\cdot}}]}{[A_{Fe^{\cdot\cdot\cdot}}]} \cdot [A_{H^{\cdot}}]$$

will have a greater value. This means that at a reduced oxygen pressure it is possible to maintain a greater ratio of $\frac{[A_{Fe^{\cdot\cdot}}]}{[A_{Fe^{\cdot\cdot\cdot}}]}$ at any pH than can be maintained under atmospheric conditions, since from (6) the $[A_{Fe^{\cdot\cdot\cdot}}]$ depends only upon the pH. This will mean that by reducing the pressure of the oxygen,

keeping the pH constant, more ferrous iron will be formed and remain in solution. This is more easily seen from the equation $\frac{[A_{Fe^{\cdot\cdot}}]}{[A_{H^{\cdot}}]^2} = \frac{4.8 \times 10^3}{[A_{O_2}]P^{\frac{1}{2}}}$ It is also evident that by increasing the pressure of the oxygen that the $[A_{Fe^{\cdot\cdot}}]$ will have to diminish. It will do so by having the ferrous iron oxidized to ferric iron and precipitated as the hydroxide.

If the pH is not kept constant and the oxygen pressure is reduced the ferrous iron concentration will increase and the hydrogen ion concentration will diminish until the new equilibrium has been reached. If the oxygen pressure is increased the reverse change will take place.

$$4\,Fe^{\cdot\cdot} + O_2 + 2\,H' \rightleftarrows 4\,Fe^{\cdot\cdot\cdot} + 2\,OH'$$

Having the above reaction at equilibrium and then increasing the pressure of oxygen the reaction will change in the direction of the upper arrow. Decreasing the oxygen pressure the reaction will go in accordance with the lower arrow until a new state of equilibrium is reached.

If complex ions of iron are formed either as ferric or ferrous it will mean that there is more iron in solution than is indicated by the above equation involving its activities. The formation of the complex ions will remove a certain portion of the ions from the sphere of activity. The ability of these complex ions to increase the solubility of the iron above that indicated in Tables II and III will depend upon how effectively the complex ions can reduce the concentration of either the ferrous or ferric ions. If the concentration of the ferrous ions is reduced below the solubility of these ions no precipitate of the hydroxide will be formed and under these conditions it will be possible to maintain high concentrations of iron in solution even under basic conditions.

Summary

From a theoretical study of transformations of iron in pure solutions equations have been developed which indicate the relationships between the activities of the ferrous, ferric, and hydrogen ions and oxygen concentration. Measurements indicate that at reactions more alkaline than pH 5.0 very small amounts of ferrous iron will occur in solution under atmospheric conditions and even smaller amounts of ferric iron are soluble.

NEW BOOKS

An Introduction to Surface Chemistry. *By Eric K. Rideal. 22 × 15 cm, pp. vii × 336. Cambridge: The University Press, 1926. Price: $5.50.* In the preface Donnan says: "The importance of an accurate study of the actions, equilibria, and structures which occur at the interfaces between homogeneous phases of matter is widely recognised at the present time. Thus a knowledge of these matters is required for a proper understanding of adsorption, the formation and stability of disperse or micro-heterogeneous systems (colloid sols and gels), catalysis, enzyme actions, etc., whilst the progress of research shows more and more clearly that the phenomena of life, i. e. the behaviour of cells and tissues, are intimately concerned with the actions occurring at surfaces, and that the effects produced by drugs, disinfectants, and other substances which profoundly affect the operation of cells and micro-organisms are largely due to surface actions."

"The great merit of Dr. E. K. Rideal's book lies in the fact that the author, whilst in no wise neglecting the thermodynamic treatment and its results, gives a very admirable account of this more recent and extremely important field of study. Since this is also the most promising line of advance in the investigation of disperse systems, Dr. Rideal's book can be most warmly recommended to all who are interested in colloid physics and chemistry. In the last two chapters the author gives a good introduction to the principal facts and theories of what is usually understood to-day as colloid chemistry, so that the reader is fully supplied with everything that is necessary for a thorough understanding of this subject. Every student and investigator of surface and colloid phenomena owes Dr. Rideal a warm debt of gratitude for his admirable survey and presentation of a great and rapidly advancing field of physico-chemical science."

The chapters are entitled: the surface tension of liquids; the surface tension of solutions; the surface films of insoluble materials; liquid-liquid interfaces; the gas-solid interface; the liquid-solid interface; differences of potential at interfaces; the conditions of stability in suspensions and emulsions; gels and hydrated colloids.

On p. 7 the author says that "for liquids which wet solids the contact angle is very nearly zero and may be taken as actually equal to zero without serious error." On p. 11 is the statement, that, in the work of Ramsay and Shields, "Ramsay did not make a sufficient allowance for the rise in the annular tube and in consequence all his values, and those of later workers who have adopted his figures for purposes of calibration for surface tensions are too low." The author does not agree with Morgan that Tate's laws hold for the falling-drop method. We are left rather up in the air as to whether one can or cannot determine molecular weights of liquids with any degree of accuracy from surface-tension measurements, pp. 25-30.

"We have noted that the Gibbs equation permits us to calculate the composition of the surface phase from a knowledge of the σ, N curve and the 'activity' of the solute in the solution; it does not however give us any information as to the thickness of the phase, beyond an indication that the liquid above the geometrical dividing surface is uniform in composition and does not acquire the characteristics of a phase in bulk. In the next chapter our attention will be devoted to the behaviour of films of insoluble substances on the surfaces of liquids and we shall have occasion to observe that we possess almost conclusive evidence that the surface phases of such films are but one molecule thick and further that the molecules of the insoluble material adsorbed on the liquid are oriented in a vertical plane; being attached to the liquid surface in the case of a complex molecule by some particular group or groups," p. 43.

When discussing the adsorption of vapors by mercury, p. 58, the author says: "It is further interesting to note that the transition from a primary adsorption film to a system in which the liquid is condensed on the mercury surface in the form of a thick layer, the free surface of which would possess the properties of the free surface of the liquid in bulk is not abrupt. We note that a point of instability is reached when the vapour pressure approaches saturation value and the apparent surface tension of the drop can fluctuate within relatively

wide limits. Iredale has shown that these values do not correspond to the tensions mercury/liquid, liquid/air, but are due to a condensed film, a secondary film on the mercury surface. Whilst the transition from the primary film to the thick layer through the formation of secondary layers takes place in this particular case within narrow limits of vapour pressure change, there is little doubt from the data that the change is definite, or that the secondary film must be built up from a great number of layers before we arrive at a film with the properties akin to those on the free surface of the liquid. This continuous change in the P,σ curves obtained by Iredale near the critical point $P_{sat.}$ appears to be similar in character to the changes, observed by Goard and Rideal, occurring in the activity, σ curves for phenol, water and salt mixtures near the salting-out point, and may be taken as evidence for a progressive thickening of the capillary layer before it acquires the properties of a bulk phase."

Under the spreading of liquids on liquids, pp. 60-86, the reviewer would have liked to have seen both a discussion and an explanation of what Gibbs has to say on this subject.

"We have noted that the adhesion of the polar groups to water and to one another is much greater than the weak adhesion of hydrocarbon chains either to water or to one another. It is thus reasonable to assume, an anticipation verified by Perrin, that soap films may be made up of composite surfaces each of which consists of two layers of oriented molecules of soap the outer surface of each side consisting of hydrocarbon chains and the polar groups held together with water as a sandwich between the oriented hydrocarbon chains. These elementary leaflets which will possess but little adhesion for one another may be built up to form thick films similar in structure to the crystalline fatty acids examined by Shearer. The leaflets may slip over one another with great ease, thus providing the play of interference colours noticed in soap films. The elementary leaflet has in fact been shown by Perrin and others to be two molecules in thickness," p. 91.

"The lubrication of metallic and other surfaces has been studied in detail by Hardy. Hardy has shown that surface spreading never occurs on solid surfaces and any spreading that does occur takes place through the vapour phase. Again, although the primary or unimolecular film is adsorbed extremely strongly to metallic surfaces when the substance contains a polar group such as the $-COOH$ or $-OH$, yet a secondary film consisting of a relatively thick multimolecular layer is generally built up. This secondary film takes a relatively long period of time to adjust itself and it appears probable that molecular orientation is proceeding in the layers of the oil at a rate much slower than for the underlying layer. On placing a load on a lubricated surface the load floats on the multimolecular layer which can be squeezed out by increasing the load until presumably a bimolecular layer with the molecules oriented towards the metal and load interface is left. The friction gradually rises as the multimolecular layer is squeezed out until it acquires a constant value dependent on the chemical constitution of the lubricant," p. 93.

The author comes out definitely in favor of the wedge theory of emulsifying agents, p. 113. "Thus the type of emulsion formed depends essentially on the relative cross-section of the non-polar and polar portions of the emulsifying agent." This statement will probably be eliminated in subsequent editions.

"A differentiation in the activities of surfaces may likewise be witnessed in a variety of chemical and catalytic processes. Thus we find that charcoal will undergo slow autoxidation when exposed to air; it will also catalytically accelerate the oxidation of a number of organic substances such as oxalic acid. By processes of selective poisoning of the charcoal it can be demonstrated quite readily that the portion of the surface which can accelerate the oxidation of oxalic acid is but a small portion of the surface which is available for say the adsorption of methylene blue and that but a minute fraction of the surface (less than 0.5% for a good sugar charcoal) is capable of undergoing autoxidation.

"Yavon and Husson have likewise clearly demonstrated the existence of patches of varying activity in platinum black showing that the progressive addition of a poison such as carbon disulphide will first inhibit the catalytic hydrogenation of substances more difficult to hydrogenate such as acetophenone without appreciably affecting the activity in respect to hydrogenation of nitrobenzene which is readily reduced," p. 143.

"The structural nature of adsorption compounds has likewise been demonstrated by Langmuir in his studies on the 'clean up' of electric lamps. Carbon monoxide was found to be strongly adsorbed at low temperature by tungsten and attempts to desorb the gas resulted in the fracture of the bonds holding the superficial tungsten atoms to the metal and the volatilisation of the whole group WCO. At higher temperatures however the W–CO union becomes weaker and the gas may be desorbed unchanged. Again he noted that small quantities of oxygen inhibit by selective adsorption the dissociation of hydrogen at the surface of a hot tungsten wire but the adsorbed oxygen is not as readily reduced as the oxide WO_3. In the case of oxygen adsorbed on charcoal the –C–O union appears to undergo a series of interesting changes. At very low temperatures according to Dewar a small fraction of oxygen may be adsorbed and desorbed from a charcoal surface, the union being apparently between the oxygen molecule and the charcoal and relatively feeble.

"At 0° to 100° C. part of the oxygen adsorbed on charcoal is endowed with catalytic properties, thus it will readily oxidise oxalic acid, amino acids, cystein and other similar compounds, whilst we would anticipate similar reactions if the oxygen molecule were now adsorbed in such a way as to cause a breakage of one of the two bonds $O=O \longrightarrow \begin{matrix} O \\ | \\ O \end{matrix} - \begin{matrix} O \\ | \\ O \end{matrix}$.

At high temperatures, as is well known, oxygen is irreversibly adsorbed by charcoal and is only desorbed in the form of the gaseous oxides of carbon. The oxygen-carbon union now exceeds in strength the union between the superficial carbon and the underlying atoms," p. 153.

It is a question whether much value is to be ascribed to Paneth's determinations of the surface of charcoal, p. 173, until we know whether the maximum adsorption of methylene bue does or does not vary with the apparent pH.

"In accordance with theoretical expectations only strongly ionising solvents exhibit marked endosmose, e. g. chloroform and benzene are practically inert whilst nitrobenzene, the alcohols and water exhibit the phenomenon to a marked extent. Of the ions adsorbed by materials constituting the diaphragms, as in the case of direct adsorption, the hydrogen and hydroxyl ions have the greatest influence. In acid solutions most diaphragm materials acquire a positive charge relative to the liquid which moves to the anode, in alkaline solutions hydroxyl ions are adsorbed and the liquid moves to the cathode being positive relative to the negatively charged diaphragm," p. 225.

The author accepts Loeb's views as to the formation of sodium gelatinate and gelatine chloride, p. 316. It is interesting to note, p. 320, that "the studies of Pauli and his coworkers, however, have revealed the fact that isohydric solutions of different acids do not effect equal combination with the isoelectric protein; relatively more acetic acid for example being combined than hydrochloric acid in isohydric solutions. Again, both the actual position of these maxima as well as the magnitudes of the viscosities observed vary much with the nature of the acid employed. Thus the relatively weak oxalic acid appears to be a much stronger acid than sulphuric acid, whilst trichloracetic acid does not differ appreciably from acetic acid in its effect on the viscosity of albumin. It is probable that the degree of solvation of the protein molecules and of the protein salts must not be regarded as constant but that they vary both with the nature of the salt and in the presence of neutral salts which exert like alcohol a desolvating action more or less complete on the solvated isoelectric protein as well as on the undissociated protein salts."

"The abnormality of the sodium soaps of the fatty acids of high molecular weight to form complexes in solution consisting of neutral colloid soap particles and of ionic micelle is to be attributed to the action of the long hydrocarbon chains, which are in themselves insoluble in water and tend to adhere to one another as the experiments of Langmuir have indicated. The detergent action and emulsifying power of soaps is likewise due to this cause. If we insert in an organic material containing hydrocarbon chains sufficiently long so as to render their mutual lateral adherence great enough to overcome in part the disintegration due to the thermal agitation, polar groups of the type $-COOX, -SO_3X, -N(CH_3)_3I$, which are sufficiently strong to immerse the hydrocarbon chains, in water, we obtain substances possessing colloidal nature; detergent action, emulsifying powers, gel and curd form-

ing properties will naturally be obtained. Such solutions, if the nonpolar portion of the molecule be too short or if too many polar groups be inserted or again if the polar medium water be replaced by one somewhat less polar such as alcohol, will no longer possess colloidal properties but will behave as true solutions."

Wilder D. Bancroft

Thermodynamics for Students of Chemistry. *By C. N. Hinshelwood. 19 × 13 cm; pp. v + 195. New York: E. P. Dutton and Company, 1926. Price: $1.80.* "The book has been developed from lectures in which I have done what I can to make the fundamental ideas of thermodynamics as clear as possible, and particularly to explain the methods by which the abstract general laws are brought to bear upon the actual problems of physics and chemistry. By the degree in which this one object is attained the book must be adjudged successful or otherwise. It seeks to contribute something to the clearing up of those difficulties in understanding the principles of an unfamiliar subject which most students of chemistry experience; and I have tried throughout to discuss in some detail precisely those points which I know to be found difficult.

"There is no advantage in presenting a formally unified system, because the laws of thermodynamics can be clothed in many forms, choice between which is entirely a matter of individual preference or of circumstances, and nobody can be at home with original literature without some acquaintance with them all. I have tried, therefore, to exemplify a number of the more important methods.

"A good deal of stress is laid, all through the book, on the interconnection between the laws of thermodynamics and the kinetic theory. This is in a sense a departure from a rigid thermodynamic method, but I think the gain in clearness is very great. I am out of sympathy with those who regard thermodynamics as a science based upon empirical laws independent of the actual nature of things. If it were not for the molecular-kinetic nature of things there is no particular reason for believing that the laws of thermodynamics would be what they are."

The chapters are entitled: introductory; applications of the first law of thermodynamics; the second law of thermodynamics and Carnot's theorem; the Gibbs-Helmholtz equation, maximum work and free energy; applications of the isothermal reversible cycle; entropy and thermodynamic functions—conditions of equilibrium; the foundations of the phase rule; the problem of chemical combination; entropy and probability.

It is an excellent thing to have a book on thermodynamics in which the illustrations are selected with reference to the needs of the chemists. There are a number of very interesting things in this book.

In one of its several forms the second law of thermodynamics states that "it is impossible to derive a continuous supply of work by utilizing the heat of bodies at uniform temperatures, these bodies remaining otherwise unchanged.

"The preceding argument might seem at first to imply that heat cannot be converted into work at all. Reflection shows that this is not a just implication. If we have a gas confined in a non-conducting cylinder by a piston, and if the pressure of the gas is greater than the external pressure, then those molecules of the gas which happen to be moving in the right direction may communicate some of their kinetic energy to the piston and enable it to move outward against the external pressure, thereby doing work. The gas molecules having lost kinetic energy, the gas is cooled. Work has therefore been done at the expense of the heat of the gas. But the essential point to notice is that the gas is changed not only in respect of having lost heat, but also in that it now occupies a larger volume. The case is fundamentally different from that of a gas, some of whose molecular kinetic energy is converted into mass kinetic energy of the whole gas, the volume remaining unchanged. Heat has been converted into work, *but something else has happened as well.* This is what we always find: there are many different devices for the conversion of heat into work, but, whatever the nature of the device may be, we always find, as a consequence of the nature of heat, that something besides the conversion must happen simultaneously; or, in thermodynamical

language, there must be '*compensation*.' In the example just given this compensation consisted in the change of volume of a gas, i. e. the movement of the molecules further apart," p. 15

"Velocities are, in a sense, things just as definite as grains of sand, and, just as it is highly improbable that a bushel of red sand and a bushel of white sand once mixed will ever become separated again by stirring, so it is equally improbable that the molecular velocities will ever divide themselves spontaneously into two groups again. The temperature having become equalised will remain equal. The passage of heat from a colder to a hotter body means that the cold body would get still colder and the hot body still hotter, which is exactly the same thing as the reversal of a previous partial equalisation of temperature. The Second Law states that this does not occur, and is thus simply asserting a necessary consequence of the molecular nature of matter and the kinetic nature of heat.

"It will be seen that the second law of thermodynamics is not absolute. There is nothing mechanically impossible in the sort of process which it rules out. The direction of motion of individual molecules changes continually in a way which, regarding large numbers of them together, we can only describe as random. It may so happen that at one instant all the molecules of a body chance to be moving in the same direction—or, what is quite sufficient, to have a common component in one direction. The body then moves off as a whole. Indeed, it is probable that if we only wait long enough something of the sort will happen. The waters of the Red Sea could have divided from natural causes; the Pyramids might have reared themselves or the Andes might have risen from the plains at the expense of molecular energy. But the extreme improbability of any of these occurrences is realised when the number of molecules in a gram molecule is known to be 6.1×10^{23}. If we reflect on the number of unsuccessful trials which would accompany one successful attempt to sort by shuffling the fifty-two cards of a pack, no surprise is felt that the second law of thermodynamics is true in practice. Calculation shows that a lead weight is not likely once in geological ages to rise a millimetre from the ground.

"But the validity of the second law depends entirely upon the smallness of molecules, and the vastness of the numbers contained in all ordinary bodies. For systems composed of limited numbers of molecules, such as small colloidal particles, the deviations from the law cease to be inappreciable. The Brownian motion is a manifestation of the transformation of molecular motion into the mass motion of a particle, and a violation of the second law. The smaller the particle the greater the motion. There is no sharp line between small colloidal particles and complex molecules. The Brownian movement is at the same time mass motion and molecular motion," p. 17.

"The quantity A, the external work performed when any physical or chemical process is carried out reversibly at constant temperature, is of great importance. As we have seen, it can often be expressed as the sum of two terms one representing the work of expansion, the second work done in other ways. If the volume of the system is unchanged at the end of the process, then the quantity A is represented by the second term only. A is called the decrease in *free energy* of the system. The system, having done work A, is thought of as being, by that much, less endowed with this property called free energy. There is a slight confusion about the use of this term as it is sometimes applied rather to the total work less the work of expansion. All that matters, however, is to be clear about the facts. We shall use the term in the sense in which it was originally introduced, namely, the maximum work at constant temperature," p. 55.

"Every process which can be devised must have the same value of A. This fact renders the value of A independent of the specific mechanism of the device, and incidentally justifies the employment of A as a measure of the difference between two states of a system.

"We may state the result in the form that the net work done in an isothermal reversible cycle is zero. This is a principle of great importance in thermodynamical calculations. It is necessary to guard against the error of supposing it to be a consequence of the conservation of energy in any way. It is a direct consequence of the second law. The first would not contradict the possibility that work might have been done at the expense of heat absorbed," p. 67.

"*Van't Hoff* showed how the tendency of a solute to diffuse could be made the basis of a thermodynamical theory of solutions. The free energy changes accompanying the dilution of a solution are calculated in terms of the osmotic pressure.

"We shall follow van't Hoff's method, despite the objection which has sometimes been raised that the osmotic pressure is not a property of fundamental importance. This objection seems to be without any validity at all. The second law of thermodynamics can be regarded as a direct consequence of the molecular-kinetic nature of matter. This molecular-kinetic nature shows itself in its most primitive form in the tendency of a solute to diffuse in solution. The osmotic pressure is the direct measure of this tendency. Thus, from the theoretical point of view, the osmotic pressure is the most fundamental property of the solution. That its practical measurement is difficult is irrelevant. Thermodynamics introduces it only in the intermediate stages of the derivations; it does not necessarily enter into the final results," p. 78.

On p. 81 the author deduces the formula $\pi M_0 = 1000\rho RT \log(p_s/p)$ where π is the osmotic pressure, M_s the molecular weight of the solvent as vapor, p_s the vapor pressure of the pure solvent, and ρ the density of the solvent in grams per cubic centimeter. "This relation between the osmotic pressure of the solution and the vapour pressures of solvent and solution holds good only when the vapour of the solvent behaves in accordance with Boyle's law. When the vapour pressure is not very large, this assumption is not far from the truth. M_s, it should be remembered, is the molecular weight of the solvent in the vapour state. This is important because the molecular weight in the vapour state usually has the simple value indicated by the chemical formula, while the actual molecular complexity of the solvent in the liquid state is often a matter of considerable doubt."

On p. 87 the author states that $(P_0 - P)/P_0 = n/N$ is "the form in which Raoult empirically established the law of vapour pressure lowering in dilute solutions." This is not the form that Hildebrand uses.

"The following difficulty is sometimes felt, and is only mentioned here because, remarkably enough, it is not confined to elementary students. If an applied hydrostatic pressure can prevent the entry of solvent, why cannot the bombardment pressure of the solute? Why in fact is the osmotic pressure not exerted the other way round? This difficulty depends of course upon a complete misunderstanding of the kinetic nature of pressure, and the explanation is simple. The difference between the bombardment pressures of the solvent on the two sides of the membrane measures its tendency to flow through, because the bombardment pressure on a given side of the membrane is proportional to the number of molecules which strike it, and therefore in turn to the number which pass through. If there is any difference on the two sides it means actually that more molecules of solvent are streaming one way than the other way. This, of course, cannot be balanced by the independent collisions of a foreign substance, the solute, on the membrane. On the other hand a hydrostatic pressure, whether exerted by a piston or by gravity, is transmitted by collisions through the solvent itself, and thus increases the actual solvent bombardment on the membrane until it is equal to the bombardment on the pure solvent side. (Incidentally the solute bombardment is also increased; by entering into refinements in the termodynamics of osmotic pressure it may indeed be shown that the osmotic pressure is in fact slightly influenced by the total hydrostatic pressure.) There is now osmotic equilibrium; but the membrane is now no longer in hydrostatic equilibrium, and unless rigidly supported would move through the liquid. The whole matter becomes clear when it is once realised that osmotic equilibrium and hydrostatic equilibrium are not consistent with one another," p. 96.

"The phase rule does not say *which* phase disappears when the temperature of a non-variant system is changed. Supposing the temperature to rise slightly above the melting point, molecules begin to leave the surface of the solid more rapidly than they return. Now, the all-important thing from the point of view of the present argument is that the *liquid is quite unaltered by a fresh influx of molecules of the same species as those of which it is already composed.* Hence the rate at which it yields molecules to the solid is unaltered. The increased rate of dissolution of the solid leads to no change in the liquid whereby the opposing

rate of solidification can be increased. There is no reaction whatever to the increased rate of melting relative to the rate of solidification. Hence the change proceeds without check until the solid has completely melted. In a precisely analogous way, in any one-component two-phase system at constant pressure, a displacement ot the temperature from the equilibrium value causes the velocity of transition of one phase into the other to become greater or less than the reverse change. The system being of one component and the pressure being constant, no concentration changes can come into play by way of counterbalancing this. Hence the system must change until one or the other of the phases has disappeared *entirely*. Other examples similar to the case of melting just described can easily be thought out, and the generality of this statement will then be clearly seen," p. 148.

"There is no sort of correlation between affinity and reactivity; it might be thought that, in general, substances with a large affinity for one another would combine more rapidly than those with little affinity, but the cursory consideration of a few cases like that of oxygen and hydrogen at ordinary temperatures soon shows that no such relation exists. The reverse is indeed very often true. It has been shown that, in the reaction $4H \rightleftarrows He$, which according to our views of atomic structure is theoretically possible, the formation of helium at equilibrium should be almost complete and that the affinity should be much greater than in any of the more ordinary chemical reactions. Yet the velocity is so small that no trace of such helium synthesis has ever been detected. This extreme instance may help to emphasise the complete lack of correlation between reactivity and affinity. Usually, however, the equilibrium point can be reached by suitable means. Therefore the discussion of equilibrium relations without reference to reactivity is quite as important as that of reaction velocity. From the practical point of view both aspects of the subject naturally have to be considered," p. 154.

The reviewer does not feel absolutely certain that "the recent work of Perrin on colloidal solutions has placed the question of the real existence of molecules beyond dispute," p. 2. In colloidal solutions we are dealing with particles and one can admit the real existence of particles without necessarily committing oneself as to molecules.

On p. 11 the author says that "temperature itself has no meaning except in its application to a system consisting of many molecules. A single molecule has no temperature." It would be just as legitimate to say that a single molecule has the temperature corresponding to its speed at any moment.

On p. 51 and elsewhere the author speaks of the Gibbs-Helmholtz equation. So far as the reviewer knows, this is an equation which Helmholtz did deduce and which Gibbs could have, and perhaps should have, deduced but did not. The error goes back to Ostwald who was advertizing Gibbs at that time.

Wilder D. Bancroft

The Problem of Physico-Chemical Periodicity. *By E. S. Hedges and J. E. Myers. Foreword by F. G. Donnan. 22 × 14 cm; pp. 95. London: Edward Arnold and Co., 1926. Price: 7 shillings, 6 pence.* In most branches of science, phenomena of a periodic or rhythmic character are of fundamental importance. In chemistry, however, unless we regard the periodic classification of the elements as coming within this category, manifestations of periodicity have usually been regarded hitherto as being of minor significance and of little theoretical interest. In the present volume the authors have attempted to collect information concerning all cases of physico-chemical periodicity which have been reported and to present it in an organised form. They have been very successful. The scope of the subject turns out to be much wider than would have been suspected and a survey of it suggests that periodicity is a property which must be reckoned with in the development of many aspects of chemical theory.

Following a brief introduction, a chapter headed 'Static Periodicity' deals with phenomena which are periodic in respect of some quantity other than time or distance and includes references to periodic changes in the properties of metals during cold-working and to the work of Holker on the periodic opacity produced in colloidal systems by adding increasing quantities of electrolyte. Under the title of 'Periodic Structures' are described

examples of the Liesegang Phenomenon, of banded structures produced in the absence of chemical reaction, of similar structures obtained in the absence of a colloidal medium and of the rhythmic crystallisation of pure substances. The theories which have been advanced to account for these various structures are discussed. Later chapters deal with processes commonly known as 'periodic reactions.' The periodic dissolution of metals, the catalytic decomposition of hydrogen peroxide and the various electrochemical periodic processes form the substance of separate chapters, which contain a valuable summary of the literature, concluding with an account of the recent investigations which the authors themselves have carried out on these processes. Examples of reaction velocity–time curves are included in the text. Among 'miscellaneous reactions' are described the periodic luminosity of phosphorus, cases of periodicity in homogeneous systems, periodic enzyme action and periodic phenomena in the absorption of gases. The book concludes with a consideration of the conditions which appear to determine the occurrence of physico-chemical periodicity in general and a theory is suggested in which these various periodic phenomena are attributed to the presence of metastable surfaces: at such surfaces it is possible that surface tension becomes a periodic function of concentration. Though this is rather vague, it suggested an interesting field for further investigation. Thus, the authors point out the possibility that catalysis may be periodic in character and that periodicity in biological processes may arise through a progressive increase in the concentration of some substance at an 'active surface' in the organism.

All references to original work are collected as a bibliography at the end of the book. This is certainly the most complete record of contributions to our knowledge of the subject. Two omissions may, however, be noticed, *viz.* the observations of Grube and Reuss on the periodic structure of copper electrodeposited from a solution containing gelatin and the work of duNoüy on the rhythmic crystallisation of sodium chloride from solutions containing colloids.

The book is well set up and the text appears to be free from printer's errors. There does not, however, seem to be any reason why the plate referring to p. 19 should face p. 30. The numerous curves are well reproduced.

H. J. T. Ellingham

The Evolution and Development of the Quantum Theory. *By N. M. Bligh. 22 × 15 cm; pp. 112. London: Edward Arnold and Co., 1926. Price: 9 shillings.* Mr. Bligh tells the story of the development of the quantum theory in simple and clear language. In the modest dimensions of a hundred pages, he introduces the reader to the ramifications of the theory and its applications to physics and chemistry. He follows in a historical sequence the development of the theory from Kirchhoff's law of cavity radiation and the empirical law of Stefan up to the modern theories of Bohr and Sommerfeld. The method of treatment is such that the reader with little mathematical knowledge can obtain a general idea of the whole field from the descriptive matter. It is not however a popular treatment of the subject in the true sense of the word, for the mathematical basis is given in some detail and is interspersed with references to the literature of the subject.

Books hitherto published on the quantum theory in the English language do not cover such a wide scope as the present volume; they are limited mainly to the modern theories of spectra, and refer but briefly to the laws of black body radiation. The first part of the present volume deals almost entirely with black body radiation including chapters on the early work, Wien's law, the Rayleigh-Jeans law, and Planck's law of radiation, and also contains an elementary introduction to statistical mechanics. In the second part, the author summarises the work on Einstein's law of photochemical equivalence, atomic heats, Planck's second quantum hypothesis, the quantum theory of optical spectra, and the correspondence principle. There was urgent need for a book of its scope which would provide a connected account of the theory without entering into too great detail. It is especially welcome to the physical chemist in whose sphere the quantum theory is destined to play an ever increasing rôle. The subject matter of the book forms a connecting link between physics and chemistry including as it does sections on photochemistry, the Nernst heat theorem, etc.

These sections, which deal with practical applications of the quantum theory to chemistry could have been extended with advantage.

The book, which is excellently printed on good paper, will form a convenient basis for any one wishing to become familiar with the elements of the subject and a convenient jumping off ground for the advanced textbooks and original literature to which references and bibliography are given.

W. E. Garner

An Introduction to Physical Chemistry. *By F. B. Finter. 19×14 cm; pp. 276. London: Longmans, Green and Co., 1926. Price: 6 shillings.* The teaching of physical chemistry in the upper classes of schools is a difficult matter. Whilst the subject is undoubtedly of sufficient importance in after life to justify the expenditure of a considerable amount of time at the universities and technical schools, it is frequently assumed that it is a matter too complex to be dealt with at all at schools. This is an error, as a glance at the curriculum in pure physics and in pure chemistry of any good school will indicate. Mr. Finter's book is valuable in that it supplies the type of material which might be well emphasised in education involving both physics and chemistry in the upper science classes. To the reviewer, whose only contact with school education is in the form of scholarship examinations, the book appears excellent as far as it goes; but several criticisms might be advanced. The author expressly excludes Werner's coordination hypothesis, the phase rule, surface tension, and the laws of thermodynamics. The doctrine of valency is of such a fundamental character that the simple ideas on pp. 17-20 might well be compressed and extended in scope. Again one finds in elementary classes at the University that the concepts of allotropy and phase change are most rapidly assimilated with the aid of phase rule diagrams, the shapes of the various lines being obtained from the Clapeyron-Clausius equation, with which the student is familiar in elementary physics. Finally surface energy as an introduction to colloids is of distinct value in that it robs colloids of the mysterious forces which are always conjured up to the mind of the tyro in this field. Whilst a case may be made for the exclusion of thermodynamics, there is little doubt that a reasonable fraction of an upper form can appreciate simple proofs founded on the cycle of Carnot and can make sufficient use of the calculus to reduce mathematical proofs to clear and concise statements; this fraction is worthy of encouragement even by footnotes or appendices. A few statements in the book might be questioned, thus in the law of Guldberg and Waage the rate of reaction is proportional to the active masses of the reactants. It would be better to make this statement and subsequently define active masses for gases, weak and strong solutions and solids rather than state this law in terms of molecular concentrations which statement is only true under certain conditions.

The insertion of questions and lecture experiments at the end of each section is a thoughtful and valuable addition to the volume.

Eric K. Rideal

Gmelins Handbuch der anorganischen Chemie. *Part V. Edited by R. J. Meyer. Eighth edition. 26 × 18 cm; pp. xvi + 86. Leipzig and Berlin: Verlag Chemie, 1926. Price: 11 marks.* This number on fluorine deals with the occurrence of fluorine or fluorides in nature, with the preparation and properties of the element, and with the compounds of fluorine. While no definite statement can be made, it is believed that the free fluorine found in some fluorspars by Moissan was produced by the action of radium radiation, though this has not been duplicated in the laboratory.

The reviewer was disappointed to find no references to the action of fluorine on solutions and no suggestion that this is an interesting subject.

Wilder D. Bancroft

THE AREA OF THE INTERNAL SURFACE OF CHARCOAL AS DETERMINED BY THE ADSORPTION OF THE NORMAL ALIPHATIC ALCOHOLS FROM AQUEOUS SOLUTION

BY W. E. GARNER, D. McKIE, AND B. C. J. G. KNIGHT

In the course of experiments on the adsorption of oxygen on a charcoal surface[1] it was found that carefully purified charcoal which had been previously heated to 950° under a high vacuum adsorbed small volumes of oxygen at room temperatures with the liberation of quantities of heat greater than those given by the same volume of oxygen on conversion to carbon monoxide. In an extension of this work it has been shown that each gram of charcoal is capable of adsorbing up to 0.4 cc.[2] of oxygen with the liberation of 68 Cal. for each gram mol. of oxygen adsorbed. After repeated treatment of charcoal with oxygen, and evacuation at 950°C, the charcoal always retains the power of adsorbing this volume of oxygen with the liberation of the same quantity of heat, even at end of thirty such experiments. The same behaviour was observed with another quite different sample of charcoal.

The heat of adsorption is so large that there can be but little doubt that this oxygen has reacted chemically with the surface carbon atoms, a conclusion which is in agreement with that of Rhead and Wheeler[3].

It is a matter of some interest to determine whether this chemical change occurs over the whole of the carbon surface or is limited to certain suitably orientated carbon atoms[4]. A decision on this matter could be reached were it possible to determine the area of the charcoal used in the above experiments.

The methods which have been used hitherto for the determination of the area of porous bodies are usually based on measurements of the adsorption isotherms of substances from aqueous solution. The assumption is made that adsorption ceases with the completion of the monomolecular layer, and from the number of molecules adsorbed by unit weight of adsorbent and the approximate dimensions of an adsorbed molecule a deduction is made as to the area of the surface. This method has been tested in several cases on known areas of adsorbent and found to give results which are substantially correct.[5] Paneth and Radu[6] have applied the method to the charcoal surface, and deduce areas per gram for a sample of wood charcoal which range from 46.2 to 268.0 m^2. for different adsorbates, e.g., methylene blue, acetone, lead nitrate, etc. The wide range of these values must in part be due to the employment of unsatisfactory adsorbates. Very little attention has been paid to the nature of the adsorbed substance in these and similar investigations.

[1] Blench and Garner: J. Chem. Soc., **125**, 1288 (1924).
[2] Further volumes are adsorbed but with the liberation of much smaller quantities of heat.
[3] J. Chem. Soc., **103**, 461 (1913).
[4] Cf. Rideal and Wright: J. Chem. Soc., **127**, 1347 (1925).
[5] Euler: Z. Elektrochemie, **28**, 446 (1922); van der Grinten: J. Chim. phys., **23**, 209 (1926).
[6] Ber., **57**, 221, (1924).

In the light of recent investigations on monomolecular films, it is possible to indicate the criteria which should govern the choice of adsorbates in measurements of the areas of porous bodies. These are, (1) the longest molecular dimension should be less than half the diameter of the smallest capillary passages in the porous body into which the adsorbate can penetrate, (2) the molecules should be capable of packing easily on the surface and in such a manner that the lateral forces between the adsorbed molecules increase the

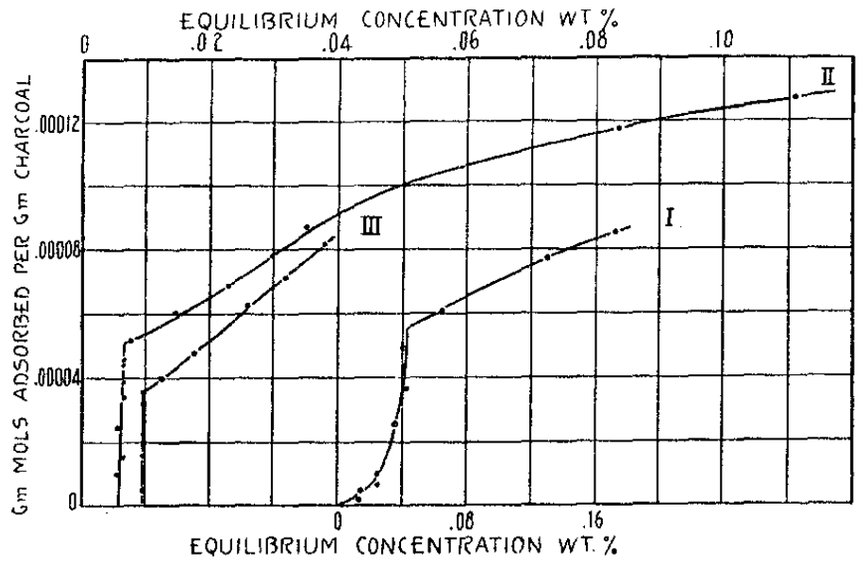


FIG. 1
I n-Propyl Alcohol
II n-Butyl Alcohol
III sec. Amyl Alcohol

stability of the film, and (3) the adsorbed molecules should be so orientated on the surface that the exposed groups of the molecules in the first layer exert weak subsidiary valency forces on the second layer; under these circumstances the tendency for the formation of the second layer will be very small.

With such adsorbates, a marked change in the character of an adsorbed film would be expected at that concentration at which the monomolecular layer is just completed. For example, the completion of the monomolecular layer should be indicated on the adsorption isotherm.

In the present investigation, the adsorption isotherms of a number of alcohols on charcoal have been investigated. These substances promised to fulfil most closely the conditions set out above. As was anticipated, a marked change in slope has been obtained at a point in the process of adsorption which very probably corresponds with the completion of the monomolecular film, (Fig 1). The curves also show evidence of the building up of a second layer which is held much less firmly than the first.

The method suggested by Donnan and Barker[1] was adopted in the determination of the adsorption isotherms. The surface tension-concentration curves of aqueous solutions of the alcohols were measured by the Jaeger bubbling method as modified by Sugden[2], over a range of concentrations from

[1] Proc. Roy. Soc., 85A, 557 (1911).
[2] J. Chem. Soc., 125, 27 (1924).

0.001 to 0.4% by weight of alcohol. From these curves and measurements of the surface tension of aqueous solutions of the alcohols when in equilibrium with charcoal, the equilibrium concentrations of the alcohol were calculated.

No difficulty was experienced in obtaining consistent values for the surface tension of aqueous solutions of the alcohols below heptyl by the above dynamical method. In the case of heptyl alcohol however, the freshly formed surface does not reach its equilibrium value in the time taken for the formation of the bubble. Frumkin[1] has noted a similar behaviour in the case of solutions of the fatty acids when using Wilhelmy's method. He finds that while the surface tension of caprylic acid reached its equilibrium value at once, capric acid solutions showed a time lag of 15 minutes, and lauric acid solutions a lag of more than one hour.

It is uncertain however whether Sugden's method gives equilibrium values for the surface tension of aqueous solutions of the lower members of the alcohols. Morgan and Neidle[2] obtained lower values for the surface tension of iso-amyl alcohol by the drop-weight method than we find for the same concentration of secondary amyl using Sugden's method. The cause of this discrepancy is not clear but it is of small moment as far as the employment of the method for analytical purposes is concerned, since it gives reproducible experimental results.

The definite change in the slope of the adsorption isotherms of n-propyl, n-butyl, and secondary amyl alcohol, occur at 0.00052, 0.00055, and 0.00038 gm. mols. of alcohol per gram of charcoal. The break occurs at the same value for the normal alcohols but at a lower value for the secondary alcohol. The equilibrium concentration remains constant throughout the initial portions of the curves for butyl and amyl alcohols, Fig. 1.

The occurrence of adsorption in steps might be interpreted as due to the presence of capillaries in the charcoal possessing diameters varying in steps. The main objection to this view is that it affords no satisfactory explanation of the constancy of the equilibrium concentrations during the initial stages of the adsorption. To explain this in a satisfactory manner, it would be necessary for the capillary passages not only to change discontinuously from small to large diameters, but also that the smaller capillaries must be of uniform diameter throughout their length. This is very unlikely especially in a charcoal which has been subjected to the erosive action of oxygen at high temperatures.

On the other hand, the results are in complete harmony with the view that the change of slope of the adsorption corresponds with the completion of a monomolecular film on the surface of the charcoal. On this theory, the number of gm. mols. composing the completed monomolecular film should depend upon the cross section of the molecules of adsorbate. This number should be greater for the primary than for the secondary alcohols, since the former have the smaller cross section. This is found to be the case.

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[1] Z. physik. Chem., **116**, 481 (1925).
[2] J. Am. Chem. Soc., **35**, 1860 (1913).

The adsorption isotherms resemble the surface tension area curves obtained by Adam and Jessop[1] for monomolecular films of straight chain acids on water and it is probable that the horizontal portions of both sets of curves owe their existence to phenomena analogous to those occurring in certain two-component systems e.g. CaO-$CaCO_3$.

The constancy of the dissociation pressure of CaO-$CaCO_3$ systems at constant temperature was explained by Langmuir as due to the fact that the condensation of carbon dioxide molecules on the surface and their evaporation from the surface took place at the edges of islands of $CaCO_3$. A molecule of carbon dioxide on colliding with a molecule of CaO only underwent reaction when the molecule of CaO was adjacent to one of $CaCO_3$. Similarly, carbon dioxide could only evaporate from molecules of $CaCO_3$ when these were adjacent to CaO. On the basis of this mechanism it was shown that the dissociation pressure should be constant as long as both CaO and $CaCO_3$ are present. It would thus appear that the lateral forces between the carbon dioxide and the calcium carbonate molecules on the surface play an important role in determining the stability of calcium carbonate.

In adsorbed films of straight chain compounds, the lateral forces are of considerable magnitude. The molecules will tend to group themselves in 'islands' over the surface; isolated molecules being held less firmly by the surface will possess a greater solution pressure than molecules grouped together. It follows therefore that adsorption of molecules of straight chain compounds will occur most frequently on areas adjacent to those on which molecules are already adsorbed, i.e. the adsorption will be analogous to the condensation of carbon dioxide on the system, CaO-$CaCO_3$. Such a mechanism would certainly account for the constancy of the equilibrium concentration during the building up of the monomolecular layer of amyl and butyl alcohol, and also for the curved isotherm of propyl alcohol over this region, for in the case of the latter, where the lateral forces are smaller in magnitude, isolated molecules would be expected to occur more frequently on the surface. The structure of an incomplete monomolecular layer of propyl alcohol will approach that of the surface of the system, Fe_3O_4-Fe_2O_3, which does not give a constant dissociation pressure.

From the number of molecules of alcohol adsorbed at the change of slope of the adsorption isotherm, and assuming that the cross sectional area per alcohol molecule is 20.5 sq. A. U., the value found by Adams for thin films on water, the internal area of unit weight of charcoal is found to be 66 m^2. Taking the density of charcoal[2] as 1.9, it can be shown that the carbon surface is composed of approximately 1.4×10^{21} carbon atoms. The total number of carbon atoms per gm. is 5.05×10^{22}, so that the ratio of surface to total atoms is 1:36. The 'active' atoms per gm. of charcoal number 1.0×10^{19}, assuming that each oxygen molecule is held by one active atom. The ratio of 'active' atoms to the total carbon atoms is 1:5000, or one in 140 of the carbon atoms on the surface combine with oxygen to give a heat of adsorption of 68 Cal/gm. mol.

[1] Proc. Roy. Soc., **110A**, 423-441 (1926).

[2] Cude and Hulett: J. Am. Chem. Soc., **42**, 391 (1920).

It is possible that oxygen molecules will penetrate pores in the charcoal which will not admit the molecules of alcohol, in which case some of the active carbon atoms may be situated on areas not measured by the above method. This will not, however, affect the main conclusion of this paper.

This investigation thus provides very definite evidence that a small fraction of the atoms composing the internal surface of charcoal are in a highly activated state. This confirms the views of Rideal and Wright (loc. cit.) which were based on investigation of oxidation processes occurring on the charcoal surface.

No two atoms on an amorphous surface will be exactly alike as regards position or energy content; their surface energies will vary continuously from a very large value down to zero accordingly to some probability law. It is thus necessary to define precisely the lower limit for the energy of the 'active' atom. This we have done arbitrarily above in defining the 'active' carbon atoms as those which give a mean value for the heat of adsorption of oxygen of 68 Cal.

Experimental

The charcoal was that employed previously in the determinations of heats of adsorption of oxygen. It contained 0.2% of ash (chiefly silica).

The n-propyl and n-butyl alcohols were Kahlbaum preparations. They were dried over potassium carbonate and distilled, the middle constant-boiling fraction being used in the adsorption experiments. B. Pts: n-propyl alcohol, 97.5°; n-butyl alcohol 117.5° (754 mm.); secondary amyl alcohol, 127-128°; n-heptyl alcohol (Eastman Kodak Co.), 174.5° (753.5 m.m.).

Conductivity water from a metal still was found to give low values for the surface tension. It was redistilled in glass with alkaline permanganate. The capacity of the still was 2 litres. The first and last 500 cc. were rejected and the middle fraction collected in a quartz flask. This was distilled in an all quartz apparatus and stored in a stoppered quartz flask. It gave a surface tension of 72.2 dynes/cm. at 25°C. (Harkins: 72.02 dynes/cm; Bircumshaw: 72.2 dynes/cm. at 25°).

Adsorption Isotherms. 0.5 grain of alcohol was weighed into each of twelve stoppered hard glass tubes of about 75 cc capacity, which had been previously treated with hot chromic-sulphuric acid mixture, washed with the above distilled water and dried. 25 cc. of the alcoholic solutions were added to the tubes. These solutions were made up in the tubes by weighing the amounts of the specially purified water and of a standard solution of the alcohol added. The standard alcohol solutions were prepared by weighing the dry alcohol and adding water to give a convenient concentration.

The tubes containing the alcoholic solutions and charcoal were suspended in a thermostat at 25° for six days, with occasional shaking. The concentration of the solutions was found to change slowly up to the 4th day. Attempts were made to hasten the attainment of equilibrium by shaking the tubes in an air thermostat, but this had no effect on the rate of adsorption and this procedure was omitted in the later determinations.

After equilibrium had been reached, the surface tension of the solutions was determined by the Jaeger method. The bubbler devised by Sugden[1] was employed. Several capillaries were used, the instrument being calibrated each time with dry thiophene-free benzene ($\sigma = 28.23$ dynes/cm.). Great care was exercised in cleaning the bubbler and capillary. A trace of grease from the finger on the capillary invariably spoiled it by causing sticking. Hot chromic-sulphuric acid was used for cleaning; it was found better to dilute slightly the concentrated sulphuric acid.

The pressure differences for bubbling from the wide tube or from the capillary were read on an alcohol gauge by means of a cathetometer. The gauge was water jacketed, and a graph was prepared by plotting density $\times g$ against temperature. The rate of bubbling was one bubble per second, and the bubbling was not continued for any length of time to avoid loss of alcohol carried away by the air current. Three successive readings of pressure gave concordant values. Concordant values could not however be obtained for heptyl alcoholic solutions above 0.0182% by weight. Except in this case, the value for the surface tension was independent of the rate of bubbling.

The results for the surface tensions of alcoholic solutions at a number of concentrations are given in Table I.

TABLE I

Surface Tension Lowering of Water. Temp. 25°C.

n-Propyl Alcohol		n-Butyl Alcohol		Amyl Alcohol	
gms wt %	dynes/cm.	gms wt %	dynes/cm.	gms wt %	dynes/cm.
0.00	72.20	0.00	72.20	0.00	72.20
0.047	71.10	0.0209	71.60	0.0243	70.75
0.072	70.90	0.0268	71.34	0.0482	69.72
0.138	70.08	0.0576	70.52	0.0713	68.69
0.223	69.08	0.0658	70.42	0.0938	67.75
0.299	68.40	0.1048	69.04	0.1157	66.63
		0.0920	69.50	0.1369	65.58
		0.1523	67.75	0.1578	64.76
		0.1979	66.45	0.1779	63.76
		0.2624	64.69	0.1978	63.15
		0.3408	62.90	0.2168	62.33
	—	0.4136	61.47	0.2355	61.77
				0.2538	61.16

n-Heptyl Alcohol		Contd.		Contd.	
gms wt %	dynes/cm.	gms wt %	dynes/cm.	gms wt %	dynes/cm.
0.00	72.20	0.0039	71.04	0.0073	69.85
0.0010	71.87	0.0047	70.68	0.0091	69.55
0.0023	71.49	0.0065	70.18	0.0182	68.63

In Table II are given the data from the experiments with charcoal, and includes the equilibrium value for the surface tension, the equilibrium concentration, and the amount of alcohol adsorbed per gram of charcoal.

[1] J. Chem. Soc., **125**, 27 (1924).

TABLE II

Adsorption Isotherms

n-Propyl Alcohol

Surface Tension Tension dynes/cm	Equilibrium Concentration wt %	gram. mols. adsorbed per gm. charcoal
71.65	0.014	0.233×10^{-4}
71.65	0.015	0.450
71.47	0.025	0.650
71.50	0.025	0.900
71.30	0.036	2.25
71.22	0.041	4.93
71.17	0.042	3.65
70.87	0.065	6.10
70.08	0.131	7.72
69.62	0.172	8.50

n-Butyl Alcohol

Surface Tension dynes/cm.	Equilibrium Concentration wt. %	gram. mols. adsorbed per gram charcoal
72.10	0.006	0.98×10^{-4}
72.05	0.007	1.55
72.09	0.006	2.48
72.05	0.007	4.51
72.02	0.007	4.56
71.97	0.008	5.21
71.77	0.015	6.12
71.55	0.023	6.95
71.17	0.035	8.73
72.07	0.007	4.61
72.04	0.007	5.28
71.34	0.030	7.82
69.72	0.084	11.80
68.92	0.111	12.72

Amyl Alcohol

Surface Tension dynes/cm.	Equilibrium Concentration wt. %	gram. mols. adsorbed per gm. charcoal
71.44	0.01	0.522×10^{-4}
71.45	"	1.634
71.45	"	3.235
71.45	"	4.02
71.37	0.013	3.60
71.00	0.018	4.82
70.64	0.026	6.30
70.34	0.032	7.16
70.07	0.038	8.21

The slight lowering of the surface tension in the initial portions of the isotherms is not due to the abstraction of substances from the charcoal or from the glass of the containing vessel, as shown by blank experiments in which no alcohol was present. There is thus a small concentration of alcohol in equilibrium with the charcoal over this range. It is however too small to be measured accurately by the method employed.

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STUDIES IN ADSORPTION. XVIII

Coagulation of Sols by a Mixture of Electrolytes and the Phenomena of Positive and Negative Acclimatization

BY S. GHOSH AND N. R. DHAR

In the foregoing papers of this series[1] we have shown that the phenomenon of 'ionic antagonism', viz. that more of an electrolyte is necessary to coagulate a sol in presence of another electrolyte, is observable with a sol when coagulated by a mixture of electrolytes, one of which possesses an ion carrying the same charge as the sol and capable of being adsorbed by the sol. Thus we have shown that enough 'ionic antagonism' is observable when sols of prussian blue, arsenious sulphide, antimony sulphide, and mastic are coagulated by mixture of electrolytes like KCl and $BaCl_2$, KNO_3 and $CaCl_2$, because these sols are capable of adsorbing similarly charged ions like Cl', NO_3', etc. We have also shown that 'ionic antagonism' is not observed when sols of ferric hydroxide, chromium hydroxide, etc., are coagulated by mixtures like KCl and K_2SO_4, KCl and $K_2C_2O_4$, etc., simply because these sols do not appreciably adsorb similarly charged ions from KCl. On the other hand, we have shown that considerable 'ionic antagonism' exists when these hydroxide sols are coagulated by such mixtures of electrolytes as K_2SO_4 and $Al(NO_3)_3$, K_2SO_4 and $FeCl_3$, K_2SO_4 and HCl, etc., where the positively charged sol can markedly adsorb the similarly charged ions of $Al^{\cdot\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $H^{\cdot}$, etc.

In former papers we have pointed out that the abnormal behaviour of sols on dilution, viz. that more of an electrolyte is necessary to coagulate a dilute sol than a concentrated one, originates from the appreciable adsorption of similarly charged ions from the coagulating electrolytes. We have also proved that the phenomenon of acclimatization, viz. that more of an electrolyte is necessary to coagulate the sol when the addition is slow than when it is rapid, observed with some sols is also due to the adsorption of similarly charged ions from the added electrolytes. We were, therefore, led to believe that (1) abnormal dilution effect, (2) ionic antagonism, and (3) the phenomenon of acclimatization, are essentially connected and go hand in hand.

We have already reported our results on the influence of concentration of a sol on its coagulation with fifteen different sols by various electrolytes in the previous part of this series. We shall now present our results on the coagulation of some of these sols by a mixture of electrolytes. The phenomenon has also been studied for some sols and these are also recorded at their proper places.

Coagulation by mixtures of electrolytes. Ferric hydroxide sol:—

In a previous paper we have shown that well-marked 'ionic antagonism' is observed when a sol of ferric hydroxide (positive) is coagulated by such

[1] Ghosh and Dhar: J. Phys. Chem., **29**, 435, 659 (1925).

mixtures as KCl and $FeCl_3$, KCl and $Al(NO_3)_3$, K_2SO_4 and $Al(NO_3)_3$, etc. In this paper we have investigated the coagulation of the same sol with mixtures of HCl and KCl, HCl and K_2SO_4, and HCl and $K_3Fe(CN)_6$.

In Tables I-III the experimental results are given:—

TABLE I

Concentration of the sol = 1.43 grm. Fe_2O_3 per litre
Amount of sol taken each time = 2 c.c.
Volume = 6 c.c. Immediate turbidity is observed

HCl N/100 added in c.c.	KCl to coagulate in c.c.
0	0.95 of N/5
0.1	0.85 of N
0.3	1.55 "
0.5	1.85 "
0.7	1.95 "
0.9	1.95 "

TABLE II

Coagulation with K_2SO_4 in presence of HCl.

N/100 HCl added in c.c.	N/400 K_2SO_4 to coagulate in c.c.
0	0.65
0.2	0.95
0.5	1.05
0.7	1.10
0.9	1.10

TABLE III

Coagulation with $K_3Fe(CN)_6$ in presence of HCl.

N/100 HCl added in c.c.	N/400 $K_3Fe(CN)_6$ to coagulate in c.c.
0	0.70
0.2	1.95
0.4	2.00

The results given in Tables I-III prove that more marked stabilisation takes place when ferric hydroxide sol is coagulated by KCl than that observed when it is coagulated by K_2SO_4 and $K_3Fe(CN)_6$ in presence of HCl. This is, because H_2SO_4 and $H_3Fe(CN)_6$ being weaker acids than HCl, there is a diminution in $H^{\cdot}$ ion concentration in the mixture of HCl and K_2SO_4 or HCl and $K_3Fe(CN)_6$. Hence in presence of HCl the stabilization, which is a direct consequence of the adsorption of hydrogen ions, can not be developed so well when the sol is coagulated with K_2SO_4 or $K_3Fe(CN)_6$ as that observed with KCl.

Aluminium hydroxide sol.

Coagulation of the same aluminium hydroxide sol as used in the dilution experiments has been effected by various pairs of electrolytes and the results are given in Tables IV-V.

TABLE IV

Concentration of the sol = 0.60 grm. Al_2O_3 per litre.
Amount of sol taken each time = 2 c.c.
Volume = 6 c.c. Time = 1 hour.
Coagulation of aluminium hydroxide sol with a mixture of KCl and K_2SO_4.

N/10 KCl added in c.c.	N/400 K_2SO_4 for complete coagulation in c.c.			
	Observed	Calculated	Difference	% Difference
0	0.65	——	——	——
1.25	0	——	——	——
0.30	0.45	0.46	−0.01	− 2.2
0.60	0.30	0.33	−0.03	− 9.1
0.90	0.15	0.17	−0.02	−11.8

TABLE V

H/10 KCl added in c.c.	N/400 $K_2C_2O_4$ for complete coagulation in c.c.			
	Observed	Calculated	Difference	% Difference
0	1.25	——	——	——
1.25	0	——	——	——
0.3	0.85	0.95	−0.10	−10.5
0.6	0.65	0.60	+0.05	+ 8.3
0.9	0.40	0.35	+0.05	+14.3

The results in Tables IV-V show that when aluminium hydroxide sol is coagulated with mixtures of electrolytes like KCl and K_2SO_4 or KCl and $K_2C_2O_4$ practically additive amounts of K_2SO_4 or $K_2C_2O_4$ are required to coagulate the sol in presence of varying amounts of KCl. Aluminium hydroxide sol, therefore, behaves normally when coagulated by a mixture of electrolytes of varying valencies. We have already shown that aluminium hydroxide sol also behaves normally on dilution when coagulated by either univalent or bivalent or polyvalent coagulating ions.

In Tables VI-VII we shall give our results on the coagulation of aluminium hydroxide sol by KCl in presence of either HCl or $Al(NO_3)_3$:—

TABLE VI

Coagulation of aluminium hydroxide sol with KCl in presence of HCl.

N/500 HCl added in c.c.	Amount of KCl to coagulate in c.c
0	1.25 of N/10
0.1	0.25 of N
0.2	0.70 "
0.3	1.05 "
0.4	1.35 "

TABLE VII

Coagulation of aluminium hydroxide sol with KCl in presence of $Al(NO_3)_3$.

N/500 $Al(NO_3)_3$ added in c.c.	Amount of KCl to coagulate in c.c.
0	1.25 of N/10
0.1	0.30 of N
0.2	0.95 "
0.3	1.40 "
0.4	1.85 "

These results prove that the sol is markedly stabilised in presence of HCl and $Al(NO_3)_3$ and that far greater amounts of KCl are required to coagulate the sol than that required for coagulation when no HCl or $Al(NO_3)_3$ is present. These results are, therefore, in line with those obtained by us on the coagulation of ferric hydroxide sol by KCl in presence of HCl or $Al(NO_3)_3$ or $FeCl_3$ and show that like ferric hydroxide, aluminium hydroxide can appreciably adsorb positive ions like $H^{\cdot}$, $Al^{\cdot\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, etc.

One remarkable fact is, however, obvious when our results on the coagulation of ferric hydroxide and aluminium hydroxide sols by KCl in presence of HCl are compared. The amount of KCl required to coagulate a sol of ferric hydroxide in presence of 0.1 c.c. N/100 HCl is about 4.47 times greater than that of KCl required to coagulate the sol when no acid is present. On the other hand, in the presence of 0.8 c.c. of N/500 HCl, the amount of KCl required to coagulate a sol of aluminium hydroxide is 10.8 times greater than that of KCl required to coagulate the same sol in the absence of the acid. In other words, HCl exerts a greater stabilising influence on aluminium hydroxide sol than on ferric hydroxide sol.

We have already reported that aluminium hydroxide sol could not be coagulated with either HCl or $Al(NO_3)_3$, because appreciable quantities of this sol dissolve in these electrolytes at their precipitating concentrations, whilst ferric hydroxide sol could be coagulated by these electrolytes. These results throw a considerable light on the stabilisation of these sols by the adsorption of a similarly charged ion and will be discussed in a separate paper on 'ageing of sols'.

Chromium hydroxide sol (positively charged).

Weiser and collaborators[1] have shown that chromium hydroxide sol behaves normally on dilution and that the sol shows the additive relationship when coagulated by a mixture of electrolytes like KCl and K_2SO_4 or KCl and $K_2C_2O_4$.

TABLE VIII

Coagulation of chromium hydroxide sol by NaCl in presence of HCl.
Concentration of the = 3.91 grms. Cr_2O_3 per litre.
Amount of sol taken each time = 4 c.c.
Total volume = 10 c.c.; Time = 1 hour.

Amount of N/100 HCl added in c.c.	Amount of N/100 NaCl to coagulate in c.c.
0	1.55
0.1	2.20
0.2	3.25
0.3	>4.60

We have investigated the coagulation of this sol by electrolytes in presence of hydrochloric acid. The sol was prepared by adding ammonium hydroxide at the ordinary temperature to a solution of chromium chloride,

[1] J. Phys. Chem., **25**, 655, 742 (1921); **28**, 232, 1253 (1924).

till the precipitate of $Cr(OH)_3$ just appeared. The sol thus prepared was first dialysed in the cold for a week and then hot dialysis was continued for another week. The sol was free from acid but on dissolving the sol with nitric acid, a precipitate was obtained with silver nitrate, showing that chloride ion was not completely removed even by hot dialysis. In Tables VIII-IX my results are given when this sol is coagulated by NaCl and K_2SO_4 in presence of HCl:—

TABLE IX

Coagulation by K_2SO_4 in presence of HCl.

Amount of N/100 HCl added in c.c.	Amount of N/500 K_2SO_4 to coagulate in c.c.
0	2.5
0.1	2.9
0.2	3.6
0.3	4.2

The foregoing results prove that like ferric hydroxide and aluminium hydroxide sols, chromium hydroxide sol is stabilised in presence of an acid like HCl, due to the preferential adsorption of similarly charged hydrogen ions. In this case the stabilisation is much less than that observed with ferric hydroxide and aluminium hydroxide sols.

Thorium hydroxide sol.

The results in Table X have been obtained when thorium hydroxide sol is coagulated by a mixture of electrolytes:—

TABLE X

Concentration of the sol = 1.36 grms. ThO_2 per litre.
2 c.c. of the sol are taken each time.
Volume = 6 c.c.; Time = 1 hour.
Coagulation of thorium hydroxide sol with a mixture of $KBrO_3$ and K_2SO_4.

N/2.4 $KBrO_3$ added in c.c.	N/500 K_2SO_4 for complete coagulation in c.c.			
	Observed	Calculated	Difference	% Difference
0	2.40	——	——	——
2.60	0	——	——	——
0.4	1.80	2.03	−0.23	−10.3
0.8	1.55	1.66	−0.11	− 6.6
1.2	1.20	1.30	−0.10	− 7.7

These results show that additive relationships are observed when thorium hydroxide sol is coagulated with a mixture of $KBrO_3$ and K_2SO_4. It has already been shown that thorium hydroxide sol behaves normally towards dilution when coagulated by either $KBrO_3$ or K_2SO_4.

Manganese dioxide sol (negatively charged)

The results in Tables XI-XIV have been obtained when negatively charged manganese dioxide sol is coagulated by a pair of electrolytes:—

TABLE XI

Concentration of the sol = 0.80 grm. MnO_2 per litre.
Amount of sol taken each time = 2 c.c.
Volume = 8 c.c.; Time = 1 hour.
Coagulation of manganese dioxide sol with a mixture of KBr and $BaCl_2$.

N/20 KBr added in c.c.	N/500 $BaCl_2$ to complete coagulation in c.c. Observed	Calculated	Difference	% Difference
1.15	0	——	——	——
0	0.8	——	——	——
0.1	0.7	0.73	−0.03	− 4.1
0.3	0.55	0.59	−0.04	− 6.8
0.5	0.35	0.45	−0.10	−22.2
0.7	0.25	0.31	−0.06	−19.3

TABLE XII

Coagulation of manganese dioxide sol with a mixture of $BaCl_2$ and $MgCl_2$.

N/500 $MgCl_2$ added in c.c.	N/500 $BaCl_2$ to complete coagulation in c.c. Observed	Calculated	Difference	% Difference
1.25	0	——	——	——
0	0.8	——	——	——
0.2	0.65	0.67	−0.02	− 3.0
0.4	0.50	0.54	−0.04	− 7.4
0.6	0.40	0.42	−0.02	− 4.8
0.8	0.25	0.29	−0.04	−13.8

TABLE XIII

Coagulation of manganese dioxide sol with a mixture of KCl and KBr.

N/20 KCl added in c.c.	N/20 KBr for complete coagulation in c.c. Observed	Calculated	Difference	% Difference
1.15	0	——	——	——
0	1.15	——	——	——
0.1	1.00	1.05	−0.05	− 4.8
0.5	0.65	0.65	0	0
0.9	0.20	0.25	−0.05	−20

TABLE XIV

Coagulation of manganese dioxide sol with a mixture of KOH and KCl.

N/20 KOH added in c.c.	N/20 KCl for complete coagulation in c.c. Observed	Calculated	Difference	% Difference
2.8	0	——	——	——
0	1.15	——	——	——
0.3	1.50	1.04	0.46	44.2
0.7	1.6	0.86	0.74	86.0
1.1	1.5	0.70	0.80	114.3
1.5	1.35	0.53	0.82	157.7
1.9	1.15	0.37	0.78	210.8
2.3	0.60	0.21	0.39	185.7

It will be seen from Tables XI-XIV that negatively charged manganese dioxide sol behaves normally when coagulated by mixtures of KBr and $BaCl_2$, KCl and $BaCl_2$, and $MgCl_2$ and $BaCl_2$, and, therefore, additive relationships are observed when the sol is coagulated by these mixtures of electrolytes. 'Ionic antagonism' is, however, observed when the sol is coagulated by a mixture of KOH and KCl. It has been shown that appreciable amounts of OH' ions are adsorbed by manganese dioxide sol. We have already proved that comparatively greater amounts of KOH are necessary to coagulate the sol than those of other univalent anions and that the sol has a tendency to behave abnormally on dilution when coagulated by KOH. This proves that 'ionic antagonism' or more of an electrolyte is necessary to coagulate the sol in presence of an another electrolyte and abnormal dilution effect are essentially connected and go hand in hand.

Manganese dioxide sol (positively charged).

It has already been shown that this sol behaves normally on dilution when coagulated by KCl, KNO_3, K_2SO_4 etc., whilst it behaves abnormally when coagulated by $AgNO_3$ and $CuCl_2$. I have indicated that this peculiar behaviour is due to the fact that manganese dioxide sol appreciably adsorbs both $Ag^{\cdot}$ and $Cu^{\cdot\cdot}$ ions.

In Tables XV-XVII the results are given as obtained by me, when this sol is coagulated by a mixture of electrolytes:—

TABLE XV

Concentration of the sol = 0.92 grm. MnO_2 per litre.
Amount of sol taken each time = 2 c.c.
Volume = 8 c.c.; Time = 1 hour.
Coagulation with a mixture of KNO_3 and K_2SO_4

N/20 KNO_3 added in c.c.	N/1000 K_2SO_4 to complete coagulation in c.c.			
	Observed	Calculated	Difference	% Difference
1.6	0	——	——	——
0	0.8	——	——	——
0.2	0.7	0.7	0	0
0.6	0.45	0.5	−0.05	−10
1.0	0.30	0.3	0	0
1.4	0.10	0.1	0	0

TABLE XVI

Coagulation with a mixture of $CuCl_2$ and KNO_3.

Amount of N $CuCl_2$ added in c.c.	Amount of N/10 KNO_3 to coagulate in c.c.
0.65	0
0.0	0.8
0.05	2.7
0.10	2.8
0.20	2.5
0.30	2.05

TABLE XVII

Coagulation with a mixture of $AgNO_3$ and KNO_3.

Amount of N/2.725 $AgNO_3$ added in c.c.	Amount of N/10 KNO_3 to coagulate in c.c.
0	0.8
0	0.8
1.2	0
0.1	0.95
0.2	1.10
0.3	1.25
0.4	1.10
0.5	0.90
0.6	0.75

An examination of Tables XV-XVII shows that marked 'ionic antagonism' is observed when the sol is coagulated with a mixture of either $CuCl_2$ and KNO_3 or $AgNO_3$ and KNO_3, whilst additive relationships are obtained when the sol is coagulated by a mixture of KNO_3 and K_2SO_4. These results confirm our view that 'ionic antagonism' is due to the adsorption of the similarly charged cations $Ag^{\cdot}$ and $Cu^{\cdot\cdot}$ by the positively charged sol.

Vanadium pentoxide sol.

Influence of change of concentration of this sol on its coagulation has already been investigated and we have shown that this sol behaves normally towards dilution irrespective of the valency of the coagulating ion. In Table XVIII we give our results on the coagulation of this sol with a mixture of electrolytes:—

TABLE XVIII

Concentration of the sol = 0.92 grm. V_2O_5 per litre.

Amount of sol taken each time = 2 c.c.

Volume = 6 c.c.; Time = 1/2 hour.

Coagulation of vanadium pentoxide sol with a mixture of KCl and $BaCl_2$.

N/10 KCl added in c.c.	N/500 $BaCl_2$ for complete coagulation in c.c.			
	Observed	Calculated	Difference	% Difference
0	1.00	——	——	——
0.8	0	——	——	——
0.1	0.65	0.875	−0.225	−25.7
0.3	0.40	0.625	−0.225	−36.0
0.5	0.30	0.375	−0.075	−20.0

The results in Table XVIII show that the sol requires slightly smaller amounts of $BaCl_2$ than the calculated amounts when it is coagulated with a mixture of KCl and $BaCl_2$. These results, therefore, prove that the behaviour of this sol is normal when coagulated with a mixture of electrolytes of widely varying coagulating powers.

Stannic hydroxide sol (positively charged).

Coagulation of the same positively charged stannic hydroxide sol as used in dilution experiments has been determined by a pair of electrolytes and the following results have been obtained:—

TABLE XIX

Concentration of the sol = 3.52 grms. SnO_2 per litre.
Amount of sol taken each time = 2 c.c.
Volume = 10 c.c.; Time = 1 hour.

KCl N/500 added in c.c.	K_2SO_4 N/4,000 to complete coagulation in c.c. Observed	Calculated	Difference	% Difference
1.9	0	——	——	——
0	1.20	——	——	——
0.1	0.90	1.14	−0.24	−21.1
0.4	0.80	0.95	−0.15	−15.8
0.7	0.65	0.76	−0.11	−14.5
1.0	0.55	0.57	−0.02	− 3.5

When positively charged stannic hydroxide sol is coagulated by a mixture of KCl and K_2SO_4 slightly smaller quantities of K_2SO_4 are required to coagulate the sol than the calculated amounts. In other words, this sol, which we have already proved to behave normally on dilution towards its coagulation by various electrolytes, also behaves normally when coagulated by a mixture of electrolytes of varying valencies.

Uranium ferrocyanide sol.

It has already been shown that this sol has a tendency to behave normally on dilution towards all electrolytes except with potassium ferrocyanide, because ferrocyanide ions are appreciably adsorbed by the sol.

In Tables XX-XXII the results are given when this sol is coagulated by a mixture of electrolytes:—

TABLE XX

Concentration of the sol = 2.09 grms. of uranium ferrocyanide per litre.
Amount of sol taken each time = 3 c.c.
Volume = 10 c.c.; Time = 2 hours.
Coagulation with a mixture of KCl and $BaCl_2$.

N KCl added in c.c.	N/25 $BaCl_2$ for complete coagulation in c.c. Observed	Calculated	Difference	% Difference
0	1.2	——	——	——
1.8	0	——	——	——
0.2	1.1	1.06	0.04	3.8
0.6	0.85	0.80	0.05	6.2
1.0	0.70	0.53	0.17	32.1
1.40	0.35	0.26	0.09	34.6

TABLE XXI

Coagulation with a mixture of $K_4Fe(CN)_6$ and KCl.

2N $K_4Fe(CN)_6$ added in c.c.	N KCl for complete coagulation in c.c. Observed	Calculated	Difference	% Difference
0	1.8	——	——	——
1.6	0	——	——	——
0.1	2.1	1.69	0.41	24.2
0.3	2.2	1.46	0.74	50.7
0.5	2.1	1.24	0.86	69.3
0.7	2.05	1.01	1.04	100.3
0.9	1.80	0.79	1.01	127.8
1.1	1.35	0.56	0.79	142.9
1.3	1.05	0.34	0.71	208.9

TABLE XXII

Coagulation with a mixture of $BaCl_2$ and $MgCl_2$.

N/25 $MgCl_2$ added in c.c.	N/25 $BaCl_2$ for complete coagulation in c.c. Observed	Calculated	Difference	% Difference
0	1.20	——	——	——
1.5	0	——	——	——
0.4	0.85	0.88	−0.03	−3.4
0.7	0.65	0.64	0.01	1.5
1.1	0.35	0.32	0.03	9.4

An examination of Tables XX-XXII shows that greater 'ionic antagonism' is observed when the sol is coagulated by a mixture of $K_4Fe(CN)_6$ and KCl than that observed when the sol is coagulated by a mixture of KCl and $BaCl_2$. This is because ferrocyanide ions highly stabilised uranium ferrocyanide sol due to the greater adsorption of this ion. A very interesting set of results is obtained when a dilute sol of uranium ferrocyanide is coagulated by a mixture of $K_4Fe(CN)_6$ and KCl, Table XXIII.

TABLE XXIII

Coagulation of a dilute sol with a mixture of $K_4Fe(CN)_6$ and KCl.

Amount of sol taken each time = 1 c.c.

Volume = 10 c.c.; Time = 2 hours.

2N $K_4Fe(CN)_6$ added in c.c.	N KCl to complete coagulation in c.c. Observed	Calculated	Difference	% Difference
0	1.8	——	——	—
1.8	0	——	——	——
0.1	2.20	1.70	0.5	29.4
0.3	2.35	1.50	0.85	56.7
0.5	2.35	1.30	1.05	80.8
0.7	2.20	1.10	1.10	100.0
0.9	2.15	0.9	1.25	138.9
1.1	1.95	0.7	1.25	178.6
1.5	0.95	0.3	0.65	216.7
1.3	1.55	0.5	1.05	210.0

From our results on the coagulation of concentrated and diluted sols of uranium ferrocyanide with a mixture of $K_4Fe(CN)_6$ and KCl it is evident that 'ionic antagonism' is more marked in the case of the dilute sol than the concentrated one. This result is extremely important as it connects the dilution effect of a sol with the behaviour of the sol towards a mixture of electrolytes.

Gum dammar.

Coagulation of gum dammar sol with a pair of electrolytes has been studied and the results in Tables XXIV-XXV have been obtained.

TABLE XXIV

Concentration of the sol = 0.87 grm. dammarharz per litre.
Amount of sol taken each time = 2 c.c.
Volume = 10 c.c.; Time = 1 hour.
Coagulation of gum dammar sol with a mixture of KCl and $BaCl_2$.

N/2 KCl added in c.c.	N/10 $BaCl_2$ for complete coagulation in c.c.			
	Observed	Calculated	Difference	% Difference
0	1.30	——	——	——
2.60	0	——	——	——
0.20	1.40	1.20	0.20	16.7
0.60	1.30	1.00	0.30	30.0
1.00	1.15	0.80	0.35	43.8
1.40	1.00	0.60	0.40	66.7
1.80	0.70	0.40	0.30	75.0

TABLE XXV

Coagulation of gum dammar sol with a mixture of KNO_3 and $SrCl_2$.

N KNO_3 added in c.c.	N/10 $SrCl_2$ for complete coagulation in c.c.			
	Observed	Calculated	Difference	% Difference
0	1.30	——	——	——
1.20	0	——	——	——
0.10	1.40	1.19	0.21	17.6
0.30	1.30	0.98	0.32	32.6
0.50	1.15	0.76	0.39	51.3
0.70	0.90	0.54	0.36	66.7

The foregoing results show that when gum dammar sol is coagulated by mixtures of electrolytes like KCl and $BaCl_2$ or KNO_3 and $SrCl_2$ marked 'ionic antagonism' is observed. We have already shown that this sol requires greater quantities of an univalent and a bivalent cation to coagulate a dilute sol than a concentrated one.

It must be emphasised here that 'ionic antagonism' observed with a mixture of electrolytes like KCl and $BaCl_2$ with gum dammar sol is comparatively greater than that observed with mastic sol. This is because the coagulating power of $BaCl_2$ is twenty times greater than that for KCl with gum dammar sol, whilst it is only seven times greater than that for KCl with mastic sol.

Consequently, the adsorption of similarly charged Cl′ ions by gum dammar sol is more prominent with KCl than that with $BaCl_2$.

Gamboge sol.

The results in Table XXVI have been obtained when gamboge sol is coagulated with a mixture of KCl and $BaCl_2$.

TABLE XXVI

Concentration of the sol = 0.388 grm. gamboge per litre.
Amount of sol taken each time = 5 c.c.
Volume = 10 c.c.; Time = 1 hour.

2N KCl added in c.c.	N/5 $BaCl_2$ to complete coagulation in c.c.			
	Observed	Calculated	Difference	% Difference
0	0.90	——	——	——
0.90	0	——	——	——
0.10	0.95	0.80	0.15	18.8
0.20	1.00	0.70	0.30	42.9
0.30	0.85	0.60	0.25	41.7
0.40	0.75	0.50	0.25	50.0
0.50	0.60	0.40	0.20	50.0

The results in Table XXVI show that marked 'ionic antagonism' occurs when the sol is coagulated with a mixture of KCl and $BaCl_2$. The behaviour of this sol is exactly similar to that of gum dammar sol.

It has been already reported that gamboge sol behaves abnormally on dilution.

Gold sol.

Coagulation of gold sol prepared according to the method of Donau with a mixture of electrolytes has been determined by Freundlich and Scholz. They have shown that when gold sol is coagulated with mixtures of electrolytes like LiCl and KCl, LiCl and $MgCl_2$, LiCl and $BaCl_2$, and LiCl and $AlCl_3$ practically additive amounts of these electrolytes are required to coagulate the sol.

I have made some experiments on the coagulation of gold sol (prepared by Zsigmondy's method) by various pairs of electrolytes of which one has a stabilising effect. The results obtained are given in Tables XXVII-XXVIII.

TABLE XXVII

Concentration of the sol = 0.065 grm. gold per litre.
Amount of sol taken each time = 3 c.c.
Volume = 6 c.c.; Time = 1 hour.
Coagulation of gold sol with a mixture of KCl and $K_2C_2O_4$.

N/2 $K_2C_2O_4$ added in c.c.	N/2.5 KCl to complete coagulation in c.c.			
	Observed	Calculated	Difference	% Difference
0	0.90	——	——	——
1.70	0	——	——	——
0.2	1.25	0.79	0.46	58.2
0.4	1.30	0.69	0.61	88.4
0.6	1.20	0.58	0.62	107.0
0.8	0.95	0.48	0.47	98.3

TABLE XXVIII

Coagulation of gold sol with a mixture of KOH and KCl.

N/2 KOH added in c.c.	N/2.5 KCl to complete coagulation in c.c.			%
	Observed	Calculated	Difference	Difference
0	0.9	——	——	——
1.90	0	——	——	——
0.2	2.05	0.81	1.24	153
0.4	2.40	0.71	1.69	238
0.6	2.60	0.62	1.98	319
0.8	2.45	0.52	1.93	371

The results in Tables XXVII-XXVIII prove that marked 'ionic antagonism' exists when gold sol is coagulated with either a mixture of KCl and $K_2C_2O_4$ or KCl and KOH. This is because, as we have already stated, OH' and C_2O_4'' ions are appreciably adsorbed by negatively charged gold sol, which is consequently stabilised by this adsorption of ions carrying the same charge as the sol.

Silver sol.

We have determined the coagulation of silver sol prepared according to the method of Kohlschütter by various pairs of electrolytes and the results given in Table XXIX have been obtained.

TABLE XXIX

Concentration of the sol = 0.18 grm Ag per litre.

Amount of sol taken each time = 3 c.c.

Volume = 6 c.c.; Time = 1 hour.

N/8 KNO added in c.c.	N/625 $Ba(NO_3)_2$ for complete coagulation in c.c.			%
	Observed	Calculated	Difference	Difference
2.10	0	——	——	——
0	1.75	——	——	——
0.2	1.45	1.57	−0.12	−7.6
0.4	1.35	1.40	−0.05	−3.6
0.6	1.20	1.22	−0.02	−1.6

These results show that silver sol behaves normally towards a mixture of electrolytes like KNO_3 and $Ba(NO_3)_2$, but we have already observed that this sol behaves abnormally towards dilution when coagulated by KNO_3. This behaviour of silver sol on dilution is, therefore, not in agreement with our results obtained here on the coagulation of this sol with a mixture of electrolytes. We are of opinion that the abnormal behaviour observed with silver sol is not primarily due to the adsorption of similarly charged NO_3' ions from KNO_3, but due to the presence of OH' ions in the sol, which exert a great stabilising influence.

We have already shown that the abnormality of silver sol on dilution is more developed when it is coagulated with NaOH than that observed with KNO_3. We shall now show in Table XXX that in presence of OH' ions silver sol shows more abnormality on dilution towards it; coagulation with KNO_3.

TABLE XXX

Concentration of the sol = 0.08 grm. Ag per litre.
Sol A = 4 c.c. of the sol made up to 8 c.c.
Immediate colour change is observed.

Concentration of the sol	N/8 KNO_3 to coagulate in c.c.	N/8 KNO_3 to coagulate in c.c. in presence of 0.5 c.c. N/5 NaOH
A	0.80	0.70
3A/4	0.90	1.40
A/2	1.10	1.60

These results, therefore, show that the sol becomes more stable on dilution in presence of OH' ions than when no OH' ions are present.

Acclimatization

In previous papers[1] we have shown that the phenomenon of acclimatization is more developed with sols like arsenious sulphide, prussian blue, mastic, etc., than with ferric hydroxide (positive and negative) when coagulated by $KBrO_3$, $BaCl_2$, etc. On the other hand, we have observed well-marked acclimatization when a positively charged sol of ferric hydroxide is coagulated by $Al(NO_3)_3$, $FeCl_3$, etc. Moreover, we have proved that, in the coagulation of arsenious sulphide sol, *smaller* quantities of strychnine hydrochloride, quinine hydrochloride, and crystal violet are necessary to coagulate the sol when the addition is slow than when it is rapid. We have called this interesting phenomenon '*negative acclimatization*'. We have advanced a satisfactory explanation of this phenomenon as well as the phenomenon of positive acclimatization first observed by Freundlich.

In this paper we shall present the results obtained on this phenomenon with several other sols.

(1) With gum dammar sol the following results are obtained:—

When N KNO_3 is added very rapidly to 9 c.c. of the sol containing 0.483 grm of gum dammar per litre the sol requires 1.20 c.c. of the electrolyte for complete coagulation in an hour. On the other hand, when N KNO_3 is added 0.2 c.c. at a time after every twenty four hours with a shaking so as to mix up the electrolyte well, the same amount of the sol requires 1.85 c.c. of N KNO_3 for complete coagulation in one hour after the last addition of the electrolyte.

Similarly, when N/5 $SrCl_2$ is added all at once to 9 c.c. of the gum dammar sol, it requires 0.6 c.c. of the electrolyte for complete coagulation in an hour. If, however, 0.1 c.c. of the electrolyte is added every twenty four hours, the sol requires 0.8 c.c. of N/5 $SrCl_2$ to coagulate the sol completely in one hour after the last addition of the electrolyte.

Hence, it is apparent that the phenomenon of acclimatization is markedly developed when gum dammar sol is coagulated by either KNO_3 or $SrCl_2$.

(2) I have also studied the phenomenon of acclimatization when aluminium hydroxide sol is coagulated by KCl, $K_2C_2O_4$, $K_4Fe(CN)_1$ and potassium citrate. 4 c.c. of the sol containing 0.60 grm. of Al_2O_3 per litre are taken in

[1] Ghosh and Dhar: J. Phys. Chem., **29**, 435, 659 (1925); Kolloid-Z., **38**, 141 (1926).

clean test tubes and small quantities of various electrolytes are added from time to time. After each addition of the electrolytes, the test tubes are shaken to ensure mixing and complete coagulation is observed after one hour of the last addition of the electrolyte. The amounts of various electrolytes required to coagulate the same amount of the sol in an hour when added all at once were also determined. The results are given in Table XXXI.

TABLE XXXI

Electrolyte	Amount added at a time in c.c.	Amount to coagulate in c.c. (when added slowly)	Amount to coagulate in c.c. (when added all at once)
KCl N/10	0.2	1.80	1.75
$K_2C_2O_4$ N/400	0.2	1.20	1.25
$K_4Fe(CN)_1$ N/2500	0.2	1.80	1.80
K_3Cit N/2,000	0.2	1.30	1.30

The foregoing results prove that the phenomenon of acclimatization is not developed when aluminium hydroxide sol is coagulated by KCl, $K_2C_2O_4$, $K_4Fe(CN)_1$ and K_3Cit. I have already reported that this sol behaves normally towards dilution when coagulated by these electrolytes and does not show 'ionic antagonism' when coagulated by various pairs of electrolytes.

(3) The coagulation of *vanadium pentoxide sol* by the slow addition of an electrolyte has been studied. 8 c.c. of this sol containing 0.92 grm. of V_2O_5 are used and the amount of an electrolyte required to coagulate the sol completely in an hour when added drop by drop in 6 days, and that required to coagulate the same volume of the sol in an hour when the electrolyte is added all at once are also determined.

The results obtained, when vanadium pentoxide sol is coagulated by various electrolytes, are given in Table XXXII.

TABLE XXXII

Electrolyte	Amount added at a time in c.c.	Amount to coagulate when added drop by drop in six days	Amount to coagulate when added all at once
KCl N/10	0.1	1.45 c.c.	1.40 c.c.
$BaCl_2$ N/500	0.1	1.45 c.c.	1.45 c.c.
$Al(NO_3)_3$ N/1,000	0.1	0.70 c.c.	0.70 c.c.

This sol, therefore, does not show the phenomenon of acclimatization appreciably.

TABLE XXXIII

4 c.c. of gold sol containing 0.065 grm. gold per litre are used at a time.

Electrolyte	Amount added at a time in c.c.	Amount to coagulate when added drop by drop in six days	Amount to coagulate when added all at once
KCl N/5	0.2	2.00 c.c.	2.00 c.c.
$BaCl_2$ N/50	0.2	0.90 c.c.	0.95 c.c.
$K_2C_2O_4$ N/2	0.2	1.90 c.c.	1.70 c.c.
KOH N/2	0.2	2.30 c.c.	2.00 c.c.

(4) The phenomenon of acclimatization has been studied with gold sol by various electrolytes and the results are given in Table XXXIII.

It will be seen from the results in Table XXXIII that gold sol does not show any acclimatization when it is coagulated by either KCl or $BaCl_2$; on the other hand, the phenomenon is observable with either $K_2C_2O_4$ or KOH. This is because, as I have already indicated, the ions carrying the same charge as the sol are appreciably adsorbed by gold sol from $K_2C_2O_4$ or KOH.

(5) The following results have been obtained with *antimony sulphide sol* when coagulated by various electrolytes:—

5 c.c. of antimony sulphide sol containing grm. of Sb_2S_3 per litre were taken in clean test tubes and the volume was made up to 8 c.c. by adding water. The amounts of various electrolytes necessary to coagulate antimony sulphide sol by the rapid addition or slow addition were determined exactly in the same way as described for arsenious sulphide sol. The results are given in Table XXXIV

TABLE XXXIV

Electrolyte	Amount added at a time in c.c.	Amount to coagulate when added drop by drop in six days	Amount to coagulate when added all at once
KCl N/4	0.1	1.25 c.c.	1.10 c.c.
$BaCl_2$ N/100	0.1	1.65 c.c.	1.25 c.c.
Strychnine hydrochloride	0.2	1.20 c.c.	1.35 c.c.
Methylene blue	0.2	2.40 c.c.	3.50 c.c.

The sol shows the phenomenon of acclimatization when coagulated by either KCl or $BaCl_2$. On the other hand, the phenomenon of negative acclimatization is developed when the sol is coagulated by either a dye-stuff like methylene blue or an alkaloid like strychnine hydrochloride. These results are exactly similar to those obtained with arsenious sulphide sol when coagulated by dye-stuffs and alkaloids. I am of opinion that the 'negative acclimatization' shown by antimony sulphide sol when coagulated by either a dye-stuff or an alkaloid is due to the fact that just like arsenious sulphide, antimony sulphide can appreciably adsorb these substances.

(6) I have observed the phenomenon of acclimatization with negatively charged manganese dioxide sol and the results are given in Table XXXV.

TABLE XXXV

2 c.c. of the sol containing 0.81 grm. of MnO_2 per litre made up to 7 c.c.

Electrolyte	Amount added at a time in c.c.	Amount to coagulate when added in 5 days	Amount to coagulate when added rapidly
KCl N/10	0.1	1.15 c.c.	1.15 c.c.
$AgNO_3$ N/100	0.1	0.65 c.c.	0.72 cc..
$CuSO_4$ N/500	0.1	0.85 c.c.	1.05 c.c.

The phenomenon of acclimatization is not at all observed with KCl, on the other hand, the sol shows 'negative acclimatization' when coagulated by $Ag^{\cdot}$ and $Cu^{\cdot\cdot}$ ions, which are highly adsorbed.

(7) The observations on phenomenon of acclimatization studied with positively charged manganese dioxide sol are given in Table XXXVI.

TABLE XXXVI

2 c.c. of the sol containing 0.91 grm. of MnO_2 per litre made up to 7 c.c.

Electrolyte	Amount added at a time in c.c.	Amount to coagulate when added in 5 days	Amount to coagulate when added rapidly
KCl N/20	0.1	1.9 c.c.	1.8 c.c.
$AgNO_3$ N/2.725	0.1	1.45 c.c.	1.2 c.c.
$CuCl_2$ N	0.1	0.75 c.c.	0.65c.c.

It is apparent that the phenomenon of acclimatization is observed with all the three electrolytes but more markedly with Cu and Ag ions. The high adsorption of Cu and Ag ions by the positively charged manganese dioxide partially stabilises the sol. Consequently, the phenomenon of 'positive acclimatization' is observed in the coagulation of positively charged MnO_2 sol by $AgNO_3$ and $CuCl_2$.

From the researches of Freundlich[1] we know that the cations of dye-stuffs like magenta, crystal violet, etc., and cations from strychnine nitrate, quinine hydrochloride, etc., are highly adsorbed by arsenious sulphide. In other words, the ratio of the adsorption of the anions to that of the cations is extremely small. Moreover we know that the percentage of adsorption by a definite weight of an adsorbent is greater from a dilute solution than from a stronger one. Hence the amount of the adsorption of the coagulating ion is greater when the addition is dropwise than when it is added all at once, because adsorption occurs at first from a very dilute solution of the electrolytes when it is added drop by drop. It therefore follows that when the adsorption of the ion carrying the same charge as the sol is much smaller than that of the ion carrying the opposite charge, the amount of electrolyte necessary to coagulate a given amount of sol will always be less when the addition is slow than when it is rapid. On the other hand, sols like mastic, As_2S_3, prussian blue, etc., when coagulated by KCl, $BaCl_2$, etc., require larger quantities of these electrolytes when the addition is slow than when it is rapid. I have already explained this phenomenon from the point of view of adsorption of ions carrying the same charge as the sol.

I have carried on quantitative experiments on the adsorption of barium ions by arsenious sulphide sol, when the addition of the electrolyte is rapid and slow. The following results were obtained:—

40 c.c. of arsenious sulphide sol is mixed with 50 c.c. of water and 10 c.c. of $BaCl_2$ N/25 is added all at once. The mixture is shaken well and left for 24 hours, when 60 c.c. of the clear solution is taken out and the concentration of Ba ion existing in the solution is determined as $BaSO_4$. To another 40 c.c. of arsenious sulphide sol is added 50 c.c. of water and then 10 c.c. of $BaCl_2$

[1] Compare "Kapillarchemie," 582 (1921).

N/25 is added in a period of 6 days, 1 c.c. of the electrolyte being added at a time. The final concentration of Ba ion is determined from 60 c.c. of the clear solution.

In both the experiments the same pipettes and 100 c.c. flasks are used. The results given in Table XXXVII are the mean of two observations:—

TABLE XXXVII

Adsorption of Ba ion by arsenious sulphide sol from $BaCl_2$ solution.
Amount of arsenious sulphide = 0.4218 grm.
Volume = 100 c.c.

No.	Original concentration of Ba ion as $BaSO_4$	Final concentration of Ba ion as $BaSO_4$	Amount adsorbed as $BaSO_4$	Amount adsorbed as Ba in millimoles
1.	0.0467 grm. in 100 c.c.	0.0452 grm. in 100 c.c.	0.0015 grm.	0.0064
2.	do.	0.0435 grm. in 100 c.c.	0.0032 grm.	0.0137

No. 1 gives the result obtained when $BaCl_2$ solution is added rapidly, whilst No. 2 gives the result when $BaCl_2$ solution is added slowly.

It is clear from Table XXXVII that the adsorption of Ba ion is greater when the addition is slow than that when it is rapid. These results clearly show that the view advanced in this paper to explain the phenomenon of acclimatization is correct and that the explanation of Bancroft is unsound, because according to his views the adsorption of barium ion should have been *less* when the addition is slow than when it is rapid, provided the amount of electrolyte added is the same in both the cases.

From our experimental results it is, therefore, evident that sols can be divided into two distinct classes one of which is normal whilst the other class is abnormal when coagulated by a mixture of electrolytes, Table XXXVIII.

TABLE XXXVIII

Abnormal	Normal
As_2S_3, Sb_2S_3, S(Odén), prussian blue, mastic, gum dammar, and gamboge.	MnO_2 (positively and negatively charged), $Sn(OH)_4$ (positively and negatively charged), $Cr(OH)_3$ (positively and negatively charged), $Fe(OH)_3$ (positively and negatively charged), $Al(OH)_3$, $Th(OH)_4$, V_2O_5, S(Weimarn), Au, Ag, & uranium ferrocyanide.

From Table XXXVIII it will be seen that those sols, which are classed as normal follow the general dilution rule, whilst sols that are abnormal do not follow the general dilution rule. Moreover, we have shown that sols of arsenious sulphide, antimony sulphide, mastic, gum dammar, and prussian blue show the phenomenon of acclimatization markedly when coagulated by

KCl, $BaCl_2$, etc., whilst sols of ferric hydroxide positively and negatively charged, manganese dioxide positively and negatively charged, aluminium hydroxide, vanadium pentoxide and gold do not show the phenomenon appreciably when coagulated by $KBrO_3$, KCl, K_2SO_4, etc. We have therefore, suggested that (i) abnormal dilution effect (ii) abnormal behaviour when coagulated by mixtures of electrolytes of widely varying precipitating powers (iii) the phenomenon of acclimatization, and the decrease in the viscosity of a sol when small quantities of electrolytes are added, are intimately connected and go hand in hand, and are mainly due to the adsorption of an ion carrying the same charge as the sol.

With the foregoing pages were ready for communication, Weiser[1] published a paper in which he has adversely criticised our views. We shall briefly point out the weakness of Weiser's arguments and emphasise the advances made from results obtained from this laboratory in our knowledge of the phenomenon of the coagulation of sols.

We have shown that, when an ion carrying the same charge as the sol is not appreciably adsorbed, the general dilution rule is obeyed, i.e. the greater the concentration of the sol the greater is the amount of an electrolyte necessary for coagulation irrespective of the valency of the precipitating ion. This general dilution rule has been found to be applicable to sols of ferric hydroxide (positive and negative), stannic hydroxide (positive and negative), chromium hydroxide (positive and negative), manganese dioxide (positive and negative), thorium hydroxide, aluminium hydroxide, gold, sulphur (Weimarn) and vanadium pentoxide, when coagulated by such electrolytes as possess an ion carrying the same charge as the sol which is not appreciably adsorbed by the sol.

The adsorption of an ion carrying the same charge as the sol is specific and is different for different ions and sols. It must be emphasised here, therefore, that the influence of ions carrying the same charge as the sol is certainly specific and is only observable with some definite sols when coagulated by a definite electrolyte.

In a previous paper, we have shown that when ferric hydroxide sol is coagulated by KCl or $KBrO_3$ the sol follows the general dilution rule because the adsorption of the similarly charged potassium ions is not appreciable and does not interfere with the effect of the oppositely charged ions Cl' or BrO_3', and the phenomenon of coagulation observed here is a normal one. On the other hand, when ferric hydroxide sol is coagulated by either HCl or $Al(NO_3)_3$ or $FeCl_3$, besides the influence of oppositely charged ions, the effect of ions bearing the same charge as the sol is also prominent and the coagulation in this case is not so simple as with KCl or $KBrO_3$, when Cl' and BrO_3' ions bring about coagulation and the potassium ions do not appreciably interfere with the coagulation process.

Our experimental results in the coagulation of $Fe(OH)_3$ sol at various dilutions by HCl, $FeCl_3$ and $Al(NO_3)_3$ conclusively prove that in these cases the dilute sol becomes more stable than a concentrated one for these electro-

[1] J. Phys. Chem., **30**, 20 (1926).

lytes simply because the influence of similarly charged ions is very marked; on the other hand, the general dilution rule is followed by the same sol, when coagulated by either KCl or $KBrO_3$. Hence these results prove that the abnormal dilution effect is undoubtedly connected with the adsorption of the similarly charged ions, and if this influence is not appreciable, which should generally be the case, the general dilution rule is obeyed. It seems, therefore, rather peculiar that Weiser has cited these results as a serious objection to our general dilution rule, which must be obeyed by the sol in case the specific influence of ions carrying the same charge as the sol does not interfere in the coagulation of the sol by the oppositely charged ion.

From a survey of our experimental results, it will be observed that the adsorption of ions carrying the same charge as the sol is specific and is only observable with certain sols for some definite electrolytes and is not as general as the charge neutralization of a sol by the oppositely charged ions.

From some experiments on the coagulation of a few sols at various dilutions by different electrolytes Burton and Bishop[1] concluded:—

1. For univalent ions the concentration of ion necessary to produce coagulation increases with the decreasing concentration of the sol.

2. For divalent ions the concentration of ion necessary to produce coagulation is almost constant an independent of the concentration of the colloid and

3. For trivalent ions the concentration of ion necessary to produce coagulation varies almost directly with the concentration of the colloid.

In several publications we have shown that these deductions of Burton and Bishop are not generally applicable and cannot be observed with a sol which has no chemical affinity for similarly charged ions; consequently we enunciated the general dilution rule, and have completely established that the rule is strictly applicable, when the adsorption of the similarly charged ions is not appreciable and does not interfere with the effect of the oppositely charged ions. It need hardly be said here, again, that the general dilution rule is applicable not only to all sols that do not adsorb similarly charged ions appreciably but as well to those sols, which appreciably adsorb similarly charged ions, when coagulated by polyvalent precipitating ions.

Weiser has also studied the influence of dilution of a sol on its coagulation by different electrolytes and he has remarked that "if stabilising ion is adsorbed, a greater concentration of precipitating ion will be required to produce coagulation. This effect will be more pronounced the greater the dilution of the colloid, since the decreased chance both of collision and coalescence will combine to render the colloid proportionately more stable so that proportionately more of the precipitating ion must be added for complete precipitation." Thus it will be seen that Weiser has given prominence to (1) influence of similarly charged ions and (2) the increase in distance between colloid particles, in explaining the abnormal behaviour of some sols on dilution. In previous papers we have clearly shown that the increase in the dis-

[1] J. Phys. Chem., 24, 701 (1920).

tance between colloid particles on dilution can in no way explain the abnormal dilution effect. Thus we have shown, in the coagulation of arsenious sulphide sol by well-washed freshly precipitated barium sulphate, the rule that the greater the concentration of the sol, the greater the concentration of the precipitating agent, is followed, because coagulation in this case being only mechanical in nature, the question of similarly charged ions does not arise. It is rather surprising to find that Weiser in his latest paper has considered the decreased chance of collision as an important factor for the greater stability of a sol on dilution but he made the following observations in a previous paper:—"The decreased chance of collision of particles produced by diluting colloidal As_2S_3 cannot be compensated by adding an amount of KCl sufficient to precipitate the undiluted colloid and allowing to stand a reasonable time". His experiments distinctly prove that the above abnormal behaviour of arsenious sulphide when coagulated by KCl persists even when the decreased chance of coagulation is compensated by increasing the time of standing. Consequently there is a considerable confusion of thought about this point in Weiser's writings.

We have definitely proved in previous papers that when KCl, which behaves abnormally towards the coagulation of As_2S_3 and Sb_2S_3 when diluted, is used as the coagulating agent, diluted sols of the same substances do not coagulate even after the lapse of 16 hours when sufficient electrolyte is added to coagulate the concentrated sols in an hour. In the same paper we came to the conclusion that the view advanced by Kruyt and Spek, and by Mukherji and Sen that the decreased chance of collision amongst the colloidal particles is an important factor that prevents a weaker sol of arsenious sulphide from coagulating is not corroborated by experiments.

It must be remarked that Weiser has ascribed the variation of the precipitation value of an electrolyte on diluting a colloid to the relative adsorbability of the precipitating ions and the stabilising ion, without assigning definite reasons. From theoretical considerations we have concluded that the abnormal behaviour of a sol on dilution is due to the greater adsorption of the similarly charged ion by the dilute sol than the concentrated one. It has been shown that the abnormal behaviour of a sol on dilution is observed when the ratio of the adsorption of the ion carrying the same charge as the sol to that of the ion carrying the opposite charge goes on increasing as the sol is diluted. We have proved experimentally in the previous paper that positively charged manganese dioxide sol behaves abnormally on dilution when coagulated by $AgNO_3$ or $CuCl_2$, and that the ratio of the adsorption of positive ions to negative ions actually decreases with the decreasing concentration of the sol. Hence, our explanation of the abnormal behaviour of sols on dilution is not a matter of conjecture only but is supported by experimental evidence. We venture to think that this is a distinct advance in our knowledge of the phenomenon of coagulation.

We have repeatedly emphasised that the so-called 'ionic antagonism' observed when certain sols are coagulated by mixtures of electrolytes is not mainly due to the opposing influences of the coagulating ions, but is mainly

caused by the preferential adsorption of an ion carrying the same charge as the sol. Thus, we have shown that marked 'ionic antagonism' exists when arsenious sulphide, antimony sulphide, prussian blue, mastic, gamboge, gum dammar, etc. are coagulated by mixtures like KCl and $BaCl_2$, NaCl and $SrCl_2$, etc., simply because these sols are capable of adsorbing an ion carrying the same charge as the sol. In order to substantiate our views we have made further experiments in the coagulation of various other sols with a suitable pair of electrolytes, where one of them can give out such a similarly charged ion as can be appreciably adsorbed by the sols. In all cases so far studied we have found that the nature of 'ionic antagonism' is exactly similar to that observed with arsenious or antimony sulphide sols, when coagulated by KCl and $BaCl_2$, NaCl and $SrCl_2$ etc. For example, we have noted that marked 'ionic antagonism' is observed when ferric hydroxide sol (positive) is coagulated by a mixture of $Al(NO_3)_3$ and K_2SO_4; when negatively charged manganese dioxide sol is coagulated by KOH and KCl; when positively charged manganese dioxide sol is coagulated by $AgNO_3$ and KNO_3, $CuCl_2$ and KNO_3; when gold sol is coagulated by mixtures like KOH and KCl, $K_2C_2O_4$ and KCl; when uranium ferrocyanide sol is coagulated by mixtures of $K_4Fe(CN)_6$ and KCl; when sols of ferric hydroxide, chromium hydroxide, aluminium hydroxide are coagulated by mixture of HCl and KCl, HCl and K_2SO_4, etc.; when arsenious sulphide sol is coagulated by mixtures like $KHCO_3$ and KCl, $NaNO_2$ and KCl, C_6H_5COONa and KCl, $NaNO_2$ and $BaCl_2$, etc. This is certainly because stabilisation of these sols is effected by the adsorption of similarly charged ions, and in several of these cases, no ionic antagonism of the precipitating ions is possible, because the precipitating ion is the same in both the electrolytes.

It is well known that ferric hydroxide sol can appreciably adsorb $Fe^{\cdot\cdot\cdot}$ ions, negatively charged manganese dioxide sol OH' ions, positively charged manganese dioxide sol $Ag^{\cdot}$ or $Cu^{\cdot\cdot}$ ions, and gold sol C_2O_4'' or OH' ions. Moreover, we have shown that when ferric hydroxide sol is coagulated by $FeCl_3$, when positively charged manganese dioxide sol is coagulated by either $AgNO_3$ or $CuCl_2$, when negatively charged manganese dioxide sol is coagulated by KOH, or when gold sol is coagulated by either KOH or $K_2C_2O_4$, these sols show abnormal behaviour on dilution, because in these cases complication arises from the marked adsorption of ions carrying the same charge as the sols. It is, therefore, evident that the property of the sols of arsenious sulphide, antimony sulphide, prussian blue, mastic, etc, to develop 'ionic antagonism' when coagulated by mixtures of KCl and $BaCl_2$ or KCl and $SrCl_2$ is unquestionably due to the adsorption of an ion bearing the same charge as the sol. It is interesting to note that more marked 'ionic antagonism' is observed when a sol of ferric hydroxide is coagulated by $FeCl_3$ and K_2SO_4 or $Al(NO_3)_3$ and K_2SO_4 than when sols of As_2S_3, Sb_2S_3, mastic, etc, are coagulated by KCl and $BaCl_2$, KCl and $SrCl_2$, etc. This is due to the fact that the adsorption of similarly charged ions from KCl in the latter case is not so great as the adsorption of similarly charged ions like $Fe^{\cdot\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, etc, by a sol of ferric hydroxide.

In one of the communications on this subject we have shown that in the coagulation of antimony sulphide sol by a mixture of electrolytes like KCl and $BaCl_2$, the adsorption of Ba ion is markedly cut down by the presence of K ion and vice versa. An interesting fact was, however, obvious from these results that the sum of the adsorption of potassium and barium ions expressed as equivalents by Sb_2S_3 sol is greater than the adsorption of barium ion by Sb_2S_3 sol, when coagulated by $BaCl_2$ alone, but less than the adsorption of $K^{\cdot}$ ion when coagulated by only KCl. This is certainly due to the fact that more chloride ions are adsorbed by Sb_2S_3 sol when coagulated by a mixture of KCl and $BaCl_2$ than the amount adsorbed by the sol when coagulated by $BaCl_2$ alone, because the concentration of chloride ions is always greater when the sol is coagulated by a mixture of KCl and $BaCl_2$ than when $BaCl_2$ is used alone; consequently, more of the cations taken together must be required to cause complete coagulation. On the other hand, when the sol is coagulated by only KCl, the concentration of Cl' ion is always greater than its concentration when mixtures of KCl and $BaCl_2$ are used. Hence more stabilisation is observed and consequently more of the cations are necessary to bring about charge neutralisation when the sol is coagulated by KCl alone than that observed when coagulated by mixtures of KCl and $BaCl_2$.

When arsenious sulphide sol is coagulated by $BaCl_2$ alone, the concentration of the similarly charged Cl' ions being very small, they cannot exert a marked stabilising influence. On the other hand, when the sol is coagulated by KCl, the concentration of KCl necessary to coagulate the sol is far greater than that of $BaCl_2$, and consequently the concentration of Cl' ion being large in case of KCl, exert a greater stabilising influence than that observed with $BaCl_2$. Now, when a sol of As_2S_3 is coagulated by a mixture of KCl and $BaCl_2$, the concentration of Cl' ions being far greater than that when the sol is coagulated by only $BaCl_2$, more stabilisation takes place and greater amounts of $BaCl_2$ are necessary to coagulate the sol in presence of KCl. This stabilisation should increase as the concentration of Cl' ion is gradually increased by adding increasing amounts of KCl. But as a matter of fact this process cannot proceed very far as the increase in Cl' ion concentration is also associated with an increase in the concentration of potassium ions, which have a coagulating effect. If the increase in Cl' ion concentration is effected by LiCl, it is expected that greater stabilisation should be observed with this electrolyte as $Li^{\cdot}$ ion possesses smaller coagulating effect than $K^{\cdot}$ ion.

We are, therefore, of the opinion that 'ionic antagonism' observed in the coagulation of sols like arsenious sulphide, antimony sulphide by a mixture of electrolytes like KCl and $BaCl_2$ or NaCl and $SrCl_2$ is more due to the similarly charged Cl' ions, than to the cutting down of the adsorption of $Ba^{\cdot\cdot}$ or $Sr^{\cdot\cdot}$ ions by $K^{\cdot}$ or $Na^{\cdot}$ ions. In his recent paper Weiser, however, has remarked that "the greater precipitation value of $BaCl_2$ in presence of LiCl or KCl was thought to be due chiefly to the cutting down of the adsorption of each precipitating ion by the presence of the other". We, however, believe that this cutting down of adsorption can in no way explain Weiser's own results on 'ionic antagonism' with As_2S_3 sol. Thus 'ionic antagonism' observed

for the mixtures of LiCl and $BaCl_2$, NaCl and $BaCl_2$ and KCl and $BaCl_2$ is in the following order in presence of alkali chlorides, LiCl > NaCl > KCl, the maximum antagonism being observed with LiCl and the least with KCl. The experimental results of Weiser show that cutting down of adsorption of barium ions is more marked in presence of $K^{\cdot}$ ions than in presence of $Li^{\cdot}$ ions, and according to the views of Weiser the precipitating concentration of $BaCl_2$ will be less in presence of LiCl than in presence of KCl, but Weiser's own results are contrary to the above expectations. In order to explain away this anamalous behaviour Weiser has made the following remarks, "Hand in hand with this, the decrease in the adsorption of alkali by barium, which will tend to make the precipitation concentration of barium chloride higher in presence of lithium."

It is to be noted here that up till now Weiser has made no experiments in the cutting down of adsorption of alkalies by barium ions. In a previous paper we have proved that the adsorption of $K^{\cdot}$ ions is decreased to the same extent in presence of barium ions as that observed for barium ions in presence of $K^{\cdot}$ ions. It must be emphasised that as the coagulating power of $Ba^{\cdot\cdot}$ ions is about 50 times greater than that of $K^{\cdot}$ or $Li^{\cdot}$ ions, a slight difference in the cutting down of adsorption of $K^{\cdot}$ or $Li^{\cdot}$ ions in presence of $Ba^{\cdot\cdot}$ ions, should not affect the precipitation value of $BaCl_2$. Hence, we are of the opinion that the views of Weiser as quoted above are totally inadequate to explain his results. On the other hand, our explanation of this behaviour is the following and seems more sound:—

It is well known that the coagulating power of $K^{\cdot}$ ions is appreciably greater than that of $Li^{\cdot}$ ions; in other words, greater quantities of LiCl will be required than KCl to coagulate a sol of As_2S_3. Now, if the coagulation is effected by mixtures of KCl and $BaCl_2$, and LiCl and $BaCl_2$ and when the amounts of KCl and LiCl added are exactly equal, it is self-evident that the amount of $BaCl_2$ necessary to coagulate the sol will be greater in the case of LiCl than in the case of KCl.

Weiser is of the opinion that the phenomenon of 'ionic antagonism' is due more to the cutting down of adsorption of one of the precipitating ion in presence of the other, than to the adsorption of ions carrying the same charge as the sol. Moreover, he believes that the mechanism of 'ionic antagonism' observed with arsenious sulphide when coagulated by a mixture like KCl and $BaCl_2$ or LiCl and $BaCl_2$, is not of the same type as observed with ferric hydroxide sol when coagulated by a mixture $Al(NO_3)_3$ and K_2SO_4, or when cupric ferrocyanide sol is coagulated by a mixture of $K_4Fe(CN)_6$ and KCl or $BaCl_2$, or when uranium ferrocyanide sol is coagulated by a mixture of $K_4Fe(CN)_6$ and KCl. From our researches it will be absolutely clear that the nature of 'ionic antagonism' developed in all these cases is essentially the same, the only difference being that 'ionic antagonism' observed in the coagulation of ferric hydroxide sol by a mixture of $Al(NO_3)_3$ and K_2SO_4 and in ferrocyanide sols by a mixture of $K_4Fe(CN)_6$ and KCl is usually more developed than that observed in the coagulation of arsenious sulphide sol by a mixture of KCl and $BaCl_2$, simply because the adsorption of the similarly

charged ions is in larger amounts in the case of the sols of ferric hydroxide and ferrocyanide than that of Cl′ ions by arsenious sulphide.

We have already shown that the increase in the adsorption of one ion in presence of another can in no way consistently explain all the results in the coagulation of sols by a mixture of electrolytes. Moreover, we are of the opinion that this decrease in adsorption of one precipitating ion in presence of another is a general phenomenon and should be observed with all sols and freshly precipitated substances.

It seems probable that the phenomenon of cutting down of adsorption of a precipitating ion should be more pronounced with those sols or freshly precipitated substances, which are not good adsorbents than with those sols or precipitates, which are powerful adsorbents. It is well known that the phenomenon of cutting down of adsorption is readily observed with sols like As_2S_3, Sb_2S_3 and these sols cannot adsorb cations highly. On the other hand, the hydroxides of iron, chromium, aluminium are far better adsorbents of anions than these sulphides and the decrease in adsorption of one ion in presence of another is not much noticeable at small concentrations of added electrolytes with the hydroxide sols. Weiser's own experiments on the adsorption of anions by $Fe(OH)_3$ sol show that the adsorption of C_2O_4'' ion in presence of SO_4'' ion is decreased more than 30 percent as the concentration of SO_4'' ion is increased. Exactly similar results were obtained by Weiser with chromium hydroxide sol and KCl and $K_2C_2O_4$. It is well known that additive relationships are observed when ferric hydroxide sol is coagulated by a mixture of KCl and $K_2C_2O_4$, and K_2SO_4 and $K_2C_2O_4$, and chromium hydroxide sol is coagulated by KCl and $K_2C_2O_4$. We are making further experiments to show that the decrease in adsorption of a precipitating ion in presence of another is a general phenomenon and can be observable with all sols. It is, therefore, very difficult to follow the reasoning of Weiser that 'ionic antagonism', which is observed with only a few specific sols and a particular set of electrolytes, originates from a general phenomenon, viz. the cutting down of adsorption of a precipitating ion in presence of another.

We have always emphasised that the adsorption of similarly charged ions can satisfactorily explain all 'ionic antagonism' so far observed. It is, however, gratifying to observe that Weiser also emphasises the adsorption of similarly charged ions by arsenious sulphide as a fundamental factor in causing the decrease in the adsorption of a coagulating ion in presence of another, in explaining 'ionic antagonism', which is observed in the coagulation of As_2S_3 sol by KCl and $BaCl_2$, NaCl and $BaCl_2$, etc.

We are definitely of the opinion that the adsorption of ions carrying the same charge as the sol is a far more important factor than the cutting down of adsorption, as an explanation of the so-called 'ionic antagonism' when sols are coagulated by mixtures of electrolytes. We have already emphasised in the foregoing pages that the negatively charged manganese dioxide sol shows additive relationship when coagulated by mixture of electrolytes of varying valencies. Consequently, from the point of view of Weiser, who is of opinion that cutting down of the adsorption is the most important factor, when the

sol or a precipitate of manganese dioxide is treated with a mixture of either KCl and $CuCl_2$ or NH_4NO_3 and $AgNO_3$, the presence of K ions or NH_4 ions should not cut down the adsorption of $Cu^{\cdot\cdot}$ or $Ag^{\cdot}$ ions. The experimental results in Table XXXIX with precipitated manganese dioxide, however, prove that marked decrease of the adsorption of both $Cu^{\cdot\cdot}$ and $Ag^{\cdot}$ ions occurs in presence of $K^{\cdot}$ and $NH_4^{\cdot}$ ions respectively.

TABLE XXXIX

Sample of hydrated manganese dioxide contains 74% MnO_2 and 26% water.

Weight of manganese dioxide used for each adsorption experiments = 0.5 grm.

Volume = 50 c.c.

Initial concentration of the electrolytes = 10 millimoles in 50 c.c.

Electrolyte added		Amount adsorbed in millimoles	
A	B	A	B
$AgNO_3$	——	2.00	——
$AgNO_3$	NH_4NO_3	1.88	——
$CuCl_2$	——	0.82	——
——	KCl	——	1.25
$CuCl_2$	KCl	0.52	0.33

In a recent paper Weiser has shown that no 'ionic antagonism' is observed when a sol of arsenious sulphide is coagulated by a mixture of KCl and $Ce(NO_3)_3$, and he believes that this is due to the fact that the adsorption of $Ce^{\cdot\cdot\cdot}$ ions is cut down to a lesser extent in presence of $K^{\cdot}$ ions than that observed for $Ba^{\cdot\cdot}$ ions in presence of $K^{\cdot}$ ions. From the experiments of Weiser, it will be seen that the adsorption of $Ce^{\cdot\cdot\cdot}$ ions is cut down to the extent of more than 20%, when comparatively dilute solutions of KCl and $Ce(NO_3)_3$ are used. Moreover, it is expected from Weiser's line of argument that the adsorption of $K^{\cdot}$ ions should be more markedly depressed in presence of $Ce^{\cdot\cdot\cdot}$ ions than that expected in presence of $Ba^{\cdot\cdot}$ ions. It is well known that 'ionic antagonism' observed with arsenious sulphide sol for mixtures of KCl and $BaCl_2$ is sometimes as great as 90 percent, when the adsorption of $Ba^{\cdot\cdot}$ ions is cut down to an extent of 80 percent in presence of $K^{\cdot}$ ions. Hence, it appears that if simply the cutting down of adsorption were the only important factor in the coagulation of a sol by a mixture of electrolytes, 'ionic antagonism' should have been observed with mixtures of KCl and $Ce(NO_3)_3$.

We have definitely shown in previous papers that small amounts of an acid render arsenious sulphide sol unstable to a marked extent towards all electrolytes. It is well known that $Ce(NO_3)_3$ is appreciably hydrolysed and HNO_3 is set free and hence no 'ionic antagonism' is observed when the sol is coagulated by a mixture of KCl and $Ce(NO_3)_3$, because of the presence of free nitric acid, which renders the sol unstable.

It has been observed in our former papers that no 'ionic antagonism' should be developed when arsenious sulphide sol is coagulated by a mixture

of two electrolytes of similar precipitating powers. For example, no ionic antagonism is observed when arsenious sulphide sol is coagulated by a mixture like $MgCl_2$ and $BaCl_2$. When a sol of As_2S_3 is coagulated by a mixture like KCl and NaCl, it is apparent that the concentration of Cl′ ions is practically the same when the sol is coagulated by either KCl and NaCl separately or with their mixtures; consequently, it is obvious that no 'ionic antagonism' should be observed when the sol is coagulated by a mixture of KCl and NaCl. Moreover, as fairly concentrated solutions of both KCl and NaCl are used, it is evident that in their mixtures the adsorption of both K and Na ions should be markedly cut down by the presence of one another, and hence according to the views of Weiser marked 'ionic antagonism' should have been observed in these cases.

It will be interesting to point out at this place that we have observed marked 'ionic antagonism' with a sol of arsenious sulphide when coagulated by mixtures like $KHCO_3$ and KCl, KNO_2 and KCl, etc., where the cations being the same in both the cases, it is very difficult to imagine the depression of the adsorption of cations and explain 'ionic antagonism'. Similarly Mukherji and Ghosh have observed that sufficient 'ionic antagonism' also exists when arsenious sulphide sol is coagulated by a mixture of $K_4Fe(CN)_6$ and KCl. More or less similar results are obtained by Weiser in the coagulation of As_2S_3 sol with the same mixture of electrolytes. In all these cases 'ionic antagonism' developed has to be ascribed to the stabilisation of the sols by the highly adsorbed anions. We have already remarked that $Fe(CN)_6''''$ ions are more adsorbed than Cl′ ions by As_2S_3 sol.

It must be clearly stated here that the greater adsorption of $Fe(CN)_6''''$ ion or citrate ion than Cl′ ion by As_2S_3 sol originates from the chemical affinity of As_2S_3 for these anions. In a recent paper we have clearly shown that the applicability of the Schulze-Hardy law to the phenomenon of adsorption should necessarily be limited to the cases where it originates only from the electric attraction existing between the colloid particles and oppositely charged ions, and it is unwise to seek its applicability in the cases where the adsorption occurs due to the chemical affinity of the adsorbent for the adsorbing materials. It is a pity that Weiser believes that the Schulze-Hardy law should be applicable even to the adsorption of similarly charged ions by a sol.

In previous publications we have shown that the phenomenon of acclimatization, viz. that more of an electrolyte is necessary for coagulation than when it is added rapidly, is more pronounced with sols of arsenious sulphide, mastic, gum dammar, prussian blue, etc., when coagulated by KCl, $BaCl_2$, etc. On the other hand, the phenomenon of acclimatization is not observable when ferric hydroxide sol (positive) is coagulated by $KBrO_3$ and manganese dioxide sol (positive) is coagulated by KCl, whilst enough of the phenomenon of acclimatization is developed when ferric hydroxide sol is coagulated by $Al(NO_3)_3$ and manganese dioxide sol is coagulated by either $CuCl_2$ or $AgNO_3$. In order to explain these results we have emphasised that the phenomenon of acclimatization is mainly due to the adsorption of similarly

charged ions by the sol from the added electrolytes and hence the phenomenon of acclimatization is observable when a sol is coagulated by an electrolyte that can give out similarly charged ions, which are markedly adsorbed by the sol. We have found that our view is capable of explaining the observed results, and in a recent paper we have shown that the views of Freundlich, Bancroft, and Weiser on the phenomenon of acclimatization are inadequate.

In a very recent paper Weiser has cited three factors to explain the phenomenon of acclimatization, viz. (1) the extent to which the colloid undergoes fractional precipitation; (2) the adsorbing power of the precipitated colloid and (3) the adsorbability of the precipitating ions. The last factor has been recently modified to read (3) the relative adsorbability of the precipitating and stabilising ions. Weiser has recognised that strong adsorption of the stabilising ion is not essential in case there is strong adsorption of the precipitating ions during fractional agglomeration.

In a previous paper we have already shown that fractional precipitation is observable both with arsenious sulphide and ferric hydroxide sols. Moreover, it is well known that ferric hydroxide is a far better adsorbent than arsenious sulphide. Consequently, if Weiser's views (1 and 2) were correct more acclimatization should be observed with ferric hydroxide sol than that observed with arsenious sulphide sol, but experimental results show that reverse is the case.

If, however, Weiser's argument "that strong adsorption of the stabilising ion is important, *if not essential*, in case the successive dilutions of the sol by fractional precipitation is the determining factor," be correct, the phenomenon of acclimatization with arsenious sulphide sol should only be developed when the sol is coagulated by KCl, LiCl, NaCl, etc., because only with these univalent salts, greater quantities are required to coagulate a dilute sol than a concentrated one. On the other hand, from Weiser's point of view practically the same amount of $BaCl_2$ will be necessary to coagulate the sol when it is added slowly or rapidly because the coagulating power of $BaCl_2$ is independent of the concentration of the sol, whilst smaller quantities of $Al(NO_3)_3$, $Ce(NO_3)_3$, etc., should be necessary to coagulate the sol when added slowly, because it is well known that the amount of $Al(NO_3)_3$ or $Ce(NO_3)_3$ necessary to coagulate the sol decreases with the decreasing concentration of the sol. But as a matter of fact, we have shown that the phenomenon of acclimatization is developed when As_2S_3 sol is coagulated by either KCl or $BaCl_2$ or $Al(NO_3)_3$, and we are, therefore, led to conclude that Weiser's modification of the third factor causing the phenomenon of acclimatization is of no use in explaining the experimental results.

We have performed some experiments on the phenomenon of acclimatization of arsenious sulphide sol by electrolytes like strychnine hydrochloride, quinine hydrochloride, crystal violet, etc., from which the cations are highly adsorbed in comparison with that of the anions; consequently anions in these cases possess practically no effect. We have found that in all these cases investigated the amounts of the electrolytes necessary for coagulation are smaller when the addition is slow than when rapid. It will be also interesting

to point out that we observed more marked fractional precipitation when As_2S_3 sol is coagulated by quinine hydrochloride, strychnine hydrochloride, crystal violet, etc, than that observed when this sol is coagulated by KCl, $BaCl_2$, $Al(NO_3)_3$, etc. Consequently, from Weiser's view of the removal of the coagulating ion by the partly agglomerated mass, it is expected that more marked acclimatization is to be observed with strychnine hydrochloride, quinine hydrochloride, crystal violet, etc., and the phenomenon of 'negative acclimatization' viz. *less* of a coagulating ion is necessary to precipitate the sol, when the addition is slow than when it is rapid cannot be even conceived from Weiser's point of view.

Moreover, it is difficult to see how an agglomerated mass can exert an adsorbing effect greater than the sol itself. There is no doubt that colloid particles are better adsorbents than their agglomerated mass, because the surface per unit mass of the same substance is greater when it is present as small colloid particles than when it is present as a coagulated mass. Moreover, the adsorbing capacity of colloid particles is due not only to its chemical affinity but also arises from their charge.

We venture to think that our experimental results and conclusions on the phenomenon of acclimatization mark a distinct advance in explaining the phenomenon.

In this connection we should like to point out that Weiser and Nicholas show that prussian blue sol behaves normally towards dilution when coagulated by KCl. At first, we made experiments on the coagulation of prussian blue by a mixture of electrolytes like KCl and $BaCl_2$ and observed that appreciable 'ionic antagonism' existed in this case, and we could immediately predict that the conclusions of Weiser and Nicholas are incorrect and the sol should be abnormal towards dilution when coagulated by KCl, K_2SO_4, etc. Consequently, we extended our investigation on the influence of dilution of this sol towards its coagulation by KCl, $BaCl_2$ and found that the sol behaves abnormally towards dilution when coagulated by KCl. It must be said here that the sol showed positive acclimatization when coagulated by KCl, $BaCl_2$, etc., and consequently it is needless to emphasise that the three phenomena are intimately associated.

Consequently, this correlation between these diverse phenomena is of great importance, because from an investigation of one of these phenomena, one can always predict with accuracy the other two phenomena.

It has already been said that when an electrolyte, say $K_4Fe(CN)_6$, is added to a uranium ferrocyanide sol, the first effect is the adsorption of the similarly charged $Fe(CN)_6''''$ ion by the colloid particles and I have proved that this adsorption follows the general adsorption formula. If, therefore, the sol is diluted say twice, the amount of adsorption of $Fe(CN)_6''''$ ion from the same concentration of $K_4Fe(CN)_6$ is certainly greater than half, so that the amount adsorbed per unit mass of the colloid is greater with the diluted sol than that with the concentrated one. Now, if the sol of uranium ferrocyanide is coagulated with a mixture of KCl and $K_4Fe(CN)_6$ the 'ionic antagonism' which I have explained to be due to the stabilisation of the sol by the

preferential adsorption of $Fe(CN)_6''''$ ion, should be more marked with a dilute sol than with a concentrated one. Moreover, according to my view a similar behaviour is expected when the sols of arsenious sulphide, antimony sulphide, mastic, etc., are coagulated by mixtures of KCl and $BaCl_2$, LiCl and $SrCl_2$, etc., or the sols of ferric hydroxide, chromium hydroxide, etc., are coagulated by mixtures of HCl and KCl, $FeCl_3$ and KCl, $CrCl_3$ and KCl etc. My results with prussian blue and uranium ferrocyanide sols greatly strengthen my view that the dilution effect and the behaviour towards a mixture of electrolytes are essentially connected and are mainly due to the same phenomenon of the adsorption of the ions bearing the same charge as the colloid particles.

It will be interesting to note that the cataphoretic experiments on arsenious sulphide sol carried on by different investigators are in general agreement with the view that ions carrying the same charge as the sol is adsorbed by the sol and partially stabilises it. Kruyt[1], Powis[2] and others have shown that the velocity of arsenious sulphide particles sometimes increases on the addition of electrolytes like KCl. Recently Freundlich and Zeh[3] have shown with arsenious sulphide sol and potassium ferrocyanide that the velocity increases to the extent of 12%, and then steadily decreases, whilst in the case of ferric hydroxide sol with $[(NH_3)_4CO<^{NH_2}_{OH}>CO(NH_3)_4]Cl_4$ the velocity increases only 1.9 per cent on the addition of the above salt to ferric hydroxide sol. These results conclusively support my view, which I have repeatedly emphasised that arsenious sulphide is a better adsorbent for negative ions than ferric hydroxide for positive ions. Burton[4] has shown from cataphoretic experiments that the velocity of copper sol obtained by Bredig's method first increases with KCl and then decreases. Moreover, Burton and Bishop[5] have observed that this sol behaves abnormally when coagulated by KCl. I am confident, that these two phenomena are essentially connected and are certainly due to the adsorption of $K^{\cdot}$ ions by the positively charged sol, and its consequent stabilisation due to the adsorption of ions carrying the same charge as the sol.

The above results of cataphoretic experiments definitely prove that an increment of charge occurs when small quantities of electrolytes like KCl, $K_4Fe(CN)_6$, etc., are added to the sols of arsenious sulphide, copper etc. Consequently the statement of Weiser that on adding a few drops of NaCl to a sol of arsenious sulphide the stability of the sol remains unchanged is incorrect.

Summary and Conclusion

(1) Marked ionic antagonism is observed when sols of ferric hydroxide, aluminum hydroxide, and chromic hydroxide are coagulated by mixtures like HCl and KCl, HCl and K_2SO_4, HCl and $K_3Fe(CN)_6$. Moreover, experimental

[1] Kolloid-Z., **22**, 81 (1918).
[2] J. Chem. Soc., **109**, 734 (1916).
[3] Z. physik. Chem., **114**, 65 (1924).
[4] "Physical Properties of Colloidal Solutions," 167 (1921).

results have been adduced showing that the above sols are stabilised in presence of acids, due to the preferential adsorption of similarly charged hydrogen ions by the sols of $Fe(OH)_3$, $Al(OH)_3$ and $Cr(OH)_3$.

(2) Aluminium hydroxide sol does not show ionic antagonism when coagulated by KCl and K_2SO_4 or KCl and $K_2C_2O_4$, but developes well marked ionic antagonism when coagulated by KCl and $Al(NO_3)$ due to the preferential of similarly charged aluminium ions.

(3) Hydrochloric acid exerts a greater stabilising influence on aluminium hydroxide sol prepared in the cold than on a sol of ferric hydroxide prepared from boiling solution of ferric chloride. The sol prepared in the boiling condition is more aged and has lost part of its reactivity.

(4) Positively charged thorium hydroxide sol does not show ionic antagonism when coagulated by a mixture of $KBrO_3$ and K_2SO_4.

(5) Negatively charged manganese dioxide sol behaves normally when coagulated by mixtures like KCl and KBr, $BaCl_2$ and $MgCl_2$, KBr and $BaCl_2$, but shows well-marked ionic antagonism when coagulated by a mixture of KOH and KCl. It has been definitely proved that OH' ions are markedly adsorbed by manganese dioxide.

(6) Positively charged manganese dioxide sol is normal when coagulated by KNO_3 and K_2SO_4, but develops marked ionic antagonism when coagulated by such mixtures as KNO_3 and $AgNO_3$, KNO_3 and $CuCl_2$, etc. We have proved that Ag' and Cu'' ions are markedly adsorbed by MnO_2 sol.

(7) Negatively charged vanadium pentoxide sol behaves normally when coagulated by KCl and $BaCl_2$.

(8) Positively charged stannic hydroxide sol shows no ionic antagonism when coagulated by KCl and K_2SO_4.

(9) Negatively charged uranium ferrocyanide sol behaves slightly abnormally when coagulated by a mixture of KCl and $BaCl_2$, but it develops well marked ionic antagonism when coagulated by KCl and $K_4Fe(CN)_6$. This antagonism is more marked with the dilute sols of uranium ferrocyanide than with concentrated sols. This is caused by the preferential adsorption of ferrocyanide ions by the uranium ferrocyanide sol.

(10) Sols of gamboge and gum dammar behave abnormally when coagulated by KCl and $BaCl_2$. The ionic antagonism is more marked with both these sols than with mastic sol.

(11) Marked ionic antagonism has been observed when gold sol is coagulated by mixtures like KCl and $K_2C_2O_4$, KCl and KOH etc., because gold sol can adsorb negative ions like C_2O_4'', OH', etc.

(12) Silver sol behaves normally when coagulated by KNO_3 and $Ba(NO_3)_2$ but the sol becomes more stable on dilution in presence of OH' ions than when no OH' ions are present.

(13) Sols of aluminium hydroxide, vanadium pentoxide, and gold do not appreciably show the phenomenon of positive acclimatization when coagulated by the slow addition of such electrolytes as KCl, $K_2C_2O_4$, K_4Fe

$(CN)_6$, $BaCl_2$, etc., but gold sol develops marked positive acclimatization when coagulated by the slow addition of KOH or $K_2C_2O_4$, because OH' and C_2O_4'' are adsorbed by gold sol.

(14) Antimony sulphide and gum dammar sols develop acclimatization when coagulated by KCl, KNO_3, $BaCl_2$, $SrCl_2$, etc., because the ions carrying the same charge as the sol are adsorbed by antimony sulphide and gum dammar

(15) Negatively and positively charged manganese dioxide sols, do not show the phenomenon of positive acclimatization when coagulated by KCl, but the positively charged sol develops acclimatization when coagulated by $AgNO_3$ or $CuCl_2$.

(16) Antimony sulphide sol shows negative acclimatization when coagulated by strychnine hydrochloride, methylene blue, etc., and negatively charged MnO_2 sol shows the same phenomenon when coagulated by $AgNO_3$ or $CuCl_2$. This is due to the fact that the adsorption of the oppositely charged ion in these cases is very high in comparison with that of the similarly charged ion.

(17) Experiments on adsorption have been advanced supporting our view and showing the inadequacy of the views of Freundlich, Bancroft, and Weiser on acclimatization.

(18) The phenomenon of the cutting down of the adsorption of a precipitating ion due to the presence of another seems to be a general phenomenon.

(19) (i) Abnormal dilution effect, (ii) abnormal behaviour when coagulated by mixtures of electrolytes of widely varying precipitating powers, (iii) the phenomenon of positive acclimatization and (iv) the decrease in the viscosity of a sol when small quantities of electrolytes are added are intimately connected and go hand in hand and are mainly due to the adsorption of an ion carrying the same charge as the sol.

Chemical Laboratory,
University of Allahabad,
Allahabad,
July 22, 1926.

CORRESPONDING STATES FOR THE ENTROPY OF ELEMENTS

BY B. BRUŽS

The thermodynamic function entropy has gained in its usefulness for the laboratory practice mainly by the establishment of the relation of entropy to probability and by the statement of the Third Law that its value at o°K for crystalline substances is zero.

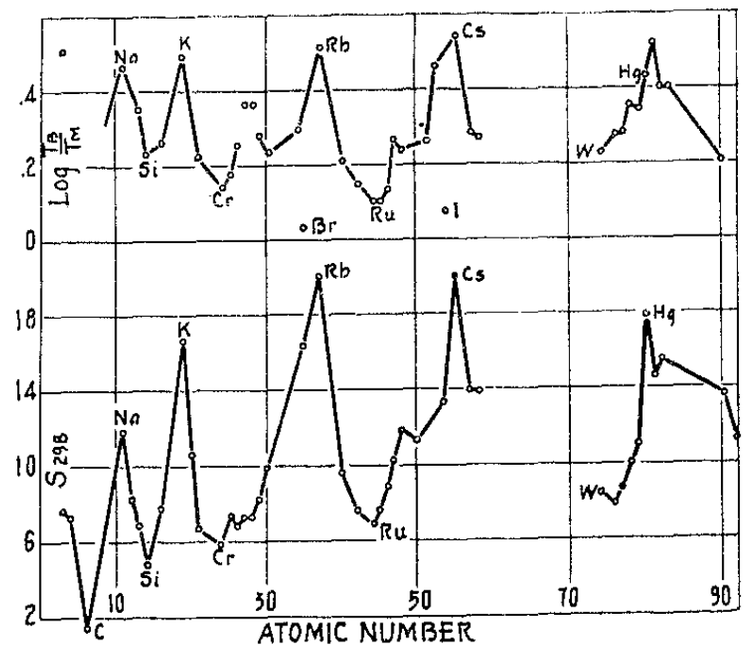


FIG. 1

The following considerations are intended to show that there is strong evidence in favour of believing that also in the field of states of aggregation the value of the absolute entropy may give some very important reference points.

Thanks to the work of Lewis, Gibson and Latimer[1] we are in possession of a fairly complete table of entropies for the elements at 298°K. It is an interesting fact that the plot of these entropies against the atomic number, Fig. 1, gives a curve which follows very closely the shape of the well known Lothar Meyer curves. In other words the entropies at 298°K are periodic functions of the atomic weight. On the other hand we know that a single temperature is a very arbitrary point for comparison, in fact a simple consideration will show that suppose we compared the atomic heats of elements at 50°K, the result would be: the specific heats of solids are periodic functions of the atomic weight. This is a statement the use of which can not be compared with the Law of Dulong and Petit.

[1] J. Am. Chem. Soc., **44**, 1008 (1922).

This leads us to the question whether there is not a more general point on the temperature scale which could be used for comparison of entropies. The melting point was selected. It must be stated however that unfortunately we are by far not always in possession of reliable data both for melting points as well as for specific heats, the two quantities necessary for our calculations. The values used in this paper are selected from Landolt and Börnstein (1923). Another unavoidable fault was the assumption of constancy of specific heats above 0°C. Considering these factors we have to count with an error of at least 10%. The entropy at the melting point was found in the following way

$$S_m = \int_0^m c_p d\ln T = \int_0^{298} c_p d\ln T + \int_{298}^m c_p d\ln T$$

or on the bases of our assumptions

$$S_m = S_{298} + 2.303\ c_p \log T_m/298$$

where the values of Lewis and coworkers are used for S_{298}. Inspecting Table I we arrive at the striking result that the values of S_m obtained in this way show a fairly constant value of about 20 entropy units within the limit of the errors of the experimental data and the calculation.

TABLE I

N		S_{298}	T_m	C_p	$S_m - S_{298}$	S_m	S_t	$\log T_b/T_m$
3	Li	7.6	463	8.5	3.7	11.3		0.51
4	Be	7.3	1500	6	9.7	17.0	2.0	
6	C	1.3	4000	$\bar{5} \div 7$	15.6	16.9		
7	N	19.	23			19.0	3.5	0.53
8	O	22.6	54			22.6	1.0	0.22
11	Na	12.2	371	7.5	1.8	14.0	1.6	0.46
12	Mg	8.3	924	8.0	9.0	17.3	2.1	0.16
13	Al	6.8	930	10.	11.2	18.0	2.8	0.35
14	Si	4.7	1700	7.	12.2	16.9		0.23
16	S	7.8	392	6.4	1.8	9.6	1.1	0.26
19	K	16.6	337	7.5	0.9	17.5	1.7	0.49
20	Ca	10.6	1083	6.8	8.8	19.4		0.13
21	Ti	6.6	2000		13.0	19.6		0.22
24	Cr	5.8	1800	7.8	14.0	19.8	1.0	0.14
25	Mn	7.3	1500	8.0	12.9	20.2	1.3	0.17
26	Fe	6.7	1800	8.0	14.3	21.2	1.5	0.25
27	Co	7.2	1720	8.0	14.1	21.3	2.0	0.36
28	Ni	7.2	1720	8.0	13.9	21.1	1.9	0.36
29	Cu	8.2	1356	7.5	11.4	19.6	1.9	0.28
30	Zn	9.8	692	7.2	6.0	15.8	2.2	0.23
34	Se	(15.6)	490	7.	3.3	18.9		0.29
35	Br	16.3	266	5.6	−0.2	16.1	4.8	0.03
37	Rb	20.	312	6.9		20.	1.7	0.51
40	Zr	9.5	2000	7.	13.3	22.8		0.21
42	Mo	7.5	2840	7.1	15.5	23.0		0.15

TABLE I (continued)

N		S_{298}	T_m	C_p	$S_m - S_{298}$	S_m	S_t	$\log T_b/T_m$
44	Ru	6.9	2700	6.2	13.5	20.4		0.1
45	Rh	7.6	2230	7.	14.0	21.6		0.1
46	Pd	8.9	1830	7.6	13.7	22.6	2.1	0.13
47	Ag	10.3	1234	7.1	10.0	20.3	2.3	0.26
48	Cd	11.8	594	8.	5.5	17.3	2.1	0.24
50	Sn	11.2	505	7.9	4.2	15.4	3.0	0.70
51	Sb	(12.2)	903	6.7	7.4	19.6		0.26
52	Te	(12.8)	575	6.4	4.6	17.2	1.6	0.46
53	I	13.3	387	7.	1.8	15.1		0.07
55	Cs	20	302	7.		20.0	1.7	0.54
57	La	13.7	1100	6.2	7.5	21.2		0.28
58	Ce	13.8	910	7.2	7.9	21.7		0.27
74	W	8.4	3660	7.5	19.0	27.4		0.23
76	Os	7.8	3000	7.	16.1	23.9		0.27
77	Ir	8.7	2600	7.7	16.6	25.3		0.28
78	Pt	10.0	2050	7.	13.5	23.5		0.35
79	Au	11.0	1340	6.2	9.3	20.3	2.3	0.34
80	Hg	17.8	234	6.6	−1.5	16.3	2.4	0.43
81	Tl	14.6	576	6.7	4.3	18.9	2.6	0.52
82	Pb	15.5	600	7.4	5.1	20.6	1.9	0.50
83	Bi	(15.2)	540	7.	4.2	19.4	4.0	0.50
90	Th	13.6	2120	6.4	12.5	26.1		
92	Ur	11.1	2100	6.7	13.0	24.1		

Note. The discrepancies in the case of S, Br and I must be due to chemical change, the same is probably true for Zn and Sn. For the values of Mo, W Ir and Th experimental data will probably be responsible. Br, I and Sn have an abnormal position also on the log T_b/T_m − N curve.

There are a few exceptions, where the value of S_m deviates from 20 more than we would expect, but most of these cases can be easily reduced to greater uncertainty of experimental data or also to the case that the elements under consideration undergo a *chemical* change; under these circumstances our generalizations could evidently not hold.

The fact of periodicity of S_{298} has been used to intrapolate the S_{298}'s for Se, Sb, Te, Bi (shown in brackets in the table)with the result that the calculated values of S_m gave good results. This example is shown to indicate the immediate usefulness of the generalization $S_m = 20$ to justify the intrapolation of entropies. Another use may be the checking of melting points where their determination presents experimental difficulties.

The Entropy of Fusion

The question of the entropy of fusion (S_f), or as it has usually been stated the constancy of AL/T_m (A—atom. weight, L latent heat of fusion) has been a matter of controversy since H. Crompton,[1] although the latter ex-

[1] For a recent discussion of the rule see A. Jouniaux: Bull., (4) **37**, 513 (1925).

pression has been occasionally used, so for instance by Born to evaluate AL from the melting point of carbon. The experimental data although very rough cast a doubt on this relation.

Our previously developed statement that $S_m = 20$ does not give a possibility to answer definitely this question, because the small value of S_f which varies between 1 and 3 entropy units is too small in comparison with the value of 20 for S_m, but several cases show that the differences of S_f and S_m compensate when we add both values. We shall therefore propose as a rule that the entropies of all elements, which do not undergo marked chemical changes are equal to 22 entropy units in the fused state at their melting points. We shall therefore call the melting point a corresponding state for the entropies.

The Entropies at the Critical Point

It is a consequence of the above statement to inquire into the question of the entropies at the critical temperature. Unfortunately we have no experimental data for the direct solution of this question. For the sake of orientation we will assume the empirical rule that $T_k = 1.55 T_{boil.\,p.}$ The entropy at the critical point will be

$$\int_0^k c_p d\ln T = S_L + 2.303\, c_p \log T_k/T_m$$

$$= 22 + 0.44\, c_p + 2.303\, c_p \log T_B/T_m$$

It has been noticed during the course of the investigation that the value of $\log T_B/T_m$ is the same periodic function of the atomic weight as in the case of S_{298} (Fig. 1). To arrive at a constant value of S_k we have to expect that c_p of the liquid will also be a periodic function of the atomic weight but with the inverted character. The few data available seem to support this assumption. In fact for K, Rb, and Cs with practically equal $\log T_B/T_m$ the atomic heat is also very nearly equal to 7.5. For Br which has a very low $\log T_B/T_m$ this value is 8.6 in support of our expectations. There is the further evidence in favour of our assumption: the fairly reliable data on the heats of evaporation show the same periodic regularities as do the atomic heats of the liquid elements.

These facts would indicate the possibility of the critical temperature being a corresponding state for entropies. An idea about its numerical value we can find by calculating it for one substance e. g. Na or K where the data are best. To avoid great uncertainty in evaluating c_p for liquids at very high temperatures we will use the safer way and base our considerations on the empirical fact that the plot of the ln p against $1/T$ is always a straight line, consequently the heat of evaporation will be the same as experimentally determined at lower temperature. Now the liquid will have to gain the entropy of evaporation plus the entropy of a gas i. e. $5 \ln T_k/T_m$ to have the same entropy as a gas at the critical point. It is easy to see that the latter quantity, unless T_k/T_B largely differs from the empirically known value of 1.55 will not vary much from 7 entropy units. On the other hand the entropies of evaporation

of Na, K, Rb, Cs and very many other metals are close to 20, which gives a total for $S_k - S_L = 27$. It must be kept in mind however that the conclusions on critical temperatures will concern metals only.

We can thus tentatively generalize our observations:

The entropies of elements are equal at the following corresponding temperatures[1]

at 0°K $(S_o = 0)$
at T, where $c_v = 3/2R$ $(S_o = 1.62)$
at the Mp., for the liquid $(S_L = 22)$
at the Crit. point $(S_k = 49)$

The known relations concerning the entropies of elements do not seem to interfere with our rule.

The entropy of a monatomic gas is $S = 5/2R\ln T - R\ln p + S_o$, where S_o has been proved by quantum theory considerations to be a function of the atomic weight (M). Since the function *f* in $T_k^{5/2}p_k = f(M)$ is unknown there is no objection to $S_k = F(M) = \text{const.}$

The same concerns Eastman's[2] relation

$$S = 3/2R \ln M + R\ln \beta^{3/2}/v + C$$

where *f* for $\beta^{3/2}/v = f(M)$ is not known.

Summary

Experimental data are tabulated for a large number of elements to show that their entropy at the melting point is 22 entropy units for the liquid phase.

The term corresponding temperatures for entropies is introduced and tentatively extended to the critical temperature.

Physical Chemistry Laboratory
University of Latvia, Riga.
January 5, 1927.

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[1] Lewis and Gibson (J. Am. Chem. Soc., **39**, 2560 (1917)) have demonstrated that at temperatures, where the value of $c_v < 6$, the entropies of solids are equal at temperatures where the c_v values are equal. This is undoubtedly true for $c_v = 3R/2$ because in this region there is no appreciable difference in c_v and c_p.

[2] J. Am. Chem. Soc., **45**, 80 (1923).

ADSORPTION BY METALLIC HYDROXIDES. PART III. ADSORPTION BY PRECIPITATED ALUMINIUM HYDROXIDE

BY KSHITISH CHANDRA SEN

In previous papers, I have studied exhaustively the behaviour of hydrous ferric oxide as an adsorbent. In the following pages, the experimental results with hydrous aluminium oxide are given.

Adsorption of Arsenious Acid

The adsorption of arsenious acid by hydrated alumina has been studied by Lockemann and Paucke[1], who have shown that arsenic, in the form of arsenite or arsenate is completely removed from a dilute solution by aluminium hydroxide at the temperature of the water bath (80-90°), but not at room temperature. When the aluminium hydroxide was precipitated at higher temperature in presence of arsenite, more adsorption was noticed than when it was precipitated in the cold, the apparent explanation being due to the difference in the nature of the precipitate formed at the two temperatures. Lockemann and Paucke were however interested in the complete separation of arsenic, and they did not carry out their experiments in details. Further, in their experiments, considerable quantities of other electrolytes were present, and hence it was thought desirable to obtain some quantitative data with freshly prepared and well washed hydrated alumina. While the manuscript of this paper was being prepared Yoe[2] published an article in which some experiments on the adsorption of arsenious acid by precipitated alumina have been made. As my experiments are however more exhaustive and differ in some respects, the full results are therefore given.

TABLE I

Adsorption of arsenious acid.
Al_2O_3 = 0.2670 gr.
Vol. = 100 cc.
Time = 20 hours; KCl = 0.05 mole per litre

	Conc. of As_2O_3 in terms of iodine N/18.65	Adsorption in terms of iodine
(1)	185.75 cc	23.25 cc
(2)	185.75 cc	23.25 cc
(3)	148.6 cc	21.1 cc
(4)	148.6 cc	21.1 cc
(5)	111.45 cc	18.45 cc
(6)	111.45 cc	18.45 cc

[1] Lockemann and Paucke: Kolloid-Z., **8**, 273 (1911).
[2] J. Am. Chem. Soc., **46**, 2390 (1924).

The experimental method employed is the same as in the case of ferric hydroxide. The alumina was precipitated in the cold from a two-normal solution of aluminium chloride by a slight excess of ammonia. The sample was partly washed by decantation, and then completely by dialysis. The same sample has been used in all the experiments given below. In order to eliminate the effect of ageing, the sample has been used after 25 days after preparation. The oxide was always kept under water.

The data in Table I were obtained to study the reproducibility of the results.

These results show that in duplicate measurements, the same values of adsorption were obtained. At this place, the effect of KCl on the final equilibrium was investigated, but it was found that KCl does not show any effect on the amount of adsorption of acids by hydrated alumina.

Effect of time. The data in Table II show the effect of time on the adsorption equilibrium.

TABLE II

Conc. of As_2O_3 in grms.	Amount adsorbed after 20 hours	Amount adsorbed after 48 hours
0.39424	0.05598	0.05598
0.29568	0.04894	0.04894

From these results, it is evident that the equilibrium has been reached within 20 hours. Yoe (loc. cit.) however found that there is a further change in the amount of adsorption after 72 hours, but he considers that this change is due to some other cause.

In Table III the results obtained with varying concentration of the arsenious acid with a fixed amount of alumina are shown.

TABLE III

Original conc. of As_2O_3 in grams	Conc. of the solution after adsorption	Adsorption in grms per gram adsorbent
0.49280	0.43110	0.2311
0.39424	0.33826	0.2096
0.29568	0.24674	0.1833
0.19712	0.15520	0.1570
0.09856	0.06899	0.1108

Effect of temperature on the adsorptive power of alumina.

The effect of heating the sample of alumina on its adsorptive power was investigated by taking 10 cc of the alumina suspension in the experimental flask, and keeping the flask in boiling water for 15 minutes. The flask was then cooled to the laboratory temperature, and the amount of adsorption of the arsenious acid was investigated in the usual way. In Table IV the results are shown.

TABLE IV

Original conc. of As_2O_3 in grms	Amount of adsorption alumina—not heated	Amount of adsorption with heated alumina
0.39424	0.05598	0.04669
0.29568	0.04894	0.03967
0.19712	0.04192	0.03130
0.09856	0.02957	0.02162

It will be thus observed that the amount of adsorption decreases appreciably when the alumina is heated before the experiment is made. The effect of heating is doubtless to change the physical nature of the precipitate.

Effect of volume—when the concentration of the arsenious acid in terms of normality is constant. The actual amount of solute is thus different, Table V.

TABLE V

Concentration of As_2O_3 = 0.19712 grm. per 100 cc.
Wt. of Al_2O_3 = 0.2670 grams.

Volume of solution	Amount adsorbed in grms
60 cc	0.03877
70 cc	0.03956
80 cc	0.04059
90 cc	0.04130
100 cc	0.04192

Effect of volume. When the amount of solute is the same in every case. The concentration in terms of normality is thus different in each case, and the sample of alumina was an old one, Table VI.

TABLE VI

Concentration of As_2O_3 = 0.2278 gr.
Wt. of Al_2O_3 = 0.2670 grams.

Volume of solution in cc	Amount adsorbed in grms
100	0.02673
90	0.02740
80	0.02808
70	0.02943
60	0.03024

From Tables V-VI it will be observed that the volume of the solution has a great effect on the actual amount of adsorption by a given weight of the adsorbent. When the normality of the acid is the same, the amount of adsorption increases with the increase in the volume of the solution, and if the amount of the solute is constant, the less the volume of the solution the greater is the amount of adsorption. These results are therefore quite similar to those obtained with ferric hydroxide and given in Tables XIV to XVIII in part I of this series of papers.

Effect of some non-electrolytes like sugar and alcohol which usually decrease the surface tension of water was also investigated. The results obtained however showed that with moderate addition of either cane sugar or alcohol, there was no change in the amount of adsorption.

In Table VII the *effect of varying the quantity of the adsorbent* on the amount of adsorption of arsenious acid is shown.

TABLE VII

Conc. of As_2O_3 = 0.19712 gr.

Amount of adsorbent in grms	Conc. of solution *after adsorption*	Amount adsorbed *per gram adsorbent*
0.2136	0.16317	0.1590
0.2670	0.15520	0.1570
0.3738	0.14326	0.1441
0.4806	0.13001	0.1396
0.6408	0.11409	0.1296
0.7476	0.10480	0.1235

Reversibility of Equilibrium.

In order to test whether the adsorption of arsenious acid by hydrated alumina is reversible or not, two sets of experiments were tried. In one set, 0.2670 gram of Al_2O_3 was treated with 50 cc of N/25.11 As_2O_3 solution and kept for 20 hours. Then 50 cc more of water was added, the mixture shaken and allowed to settle for another 20 hours. At the end of this period, the supernatant liquid was analysed. In an exactly similar experiment, the alumina was treated with 100 cc of N/50.22 As_2O_3 solution. The final concentration of the supernatant solution in both the cases was found to be N/70.41. In another set, proceeding in the same way, 50 cc of a solution of As_2O_3 N/12.55 was added, and after 20 hours another 50 cc of water. In another flask, 100 cc of N/25.1 As_2O_3 solution was added at the same time. After analysis, the concentration of the supernatant liquid in both the cases was found to be N/31.7. It was thus clear that the adsorption equilibrium in this case was perfectly reversible.

Up to this time, the adsorption of arsenious acid by hydrated alumina has been investigated. It became here a matter of interest to study the adsorption of sodium arsenite by hydrated alumina and to compare the relative adsorbability of the two substances. In Table VIII, the results obtained with sodium arsenite are shown.

TABLE VIII

Wt. of Al_2O_3 = 0.2670 gr.

Original conc. of Na arsenite in terms of I_2 N/18.65	Amount adsorbed in terms of I_2 N/18.65
148.6 cc	21.1 cc
111.45 cc	18.45 cc
74.3 cc	18.8 cc
53.7 cc	13.7 cc
37.15 cc	11.15 cc

The adsorption values have been given in terms of iodine because it was found that mainly the arsenite ion was adsorbed. In Table IX a comparative study was made of the amounts of adsorption of As_2O_3 and sodium arsenite when the original concentrations in terms of iodine are the same.

TABLE IX

Original conc. in terms of iodine N/18.65	Adsorption of As_2O_3	Adsorption of Sodium arsenite
148.6 cc	21.1 cc	21.1 cc
111.45 cc	18.45 cc	18.45 cc
74.3 cc	15.8 cc	15.8 cc
37.15 cc	11.15 cc	11.15 cc

These experimental results therefore show that with both these substances, it is the arsenite ion which is actually adsorbed and from equivalent solutions, the amount of adsorption in terms of iodine is the same. The result is therefore different from that obtained with ferric hydroxide.

Having thus studied the adsorption of arsenious acid under various change of conditions, the adsorption of other mineral and organic acids by the same sample of hydrated alumina was investigated, Tables X-XV. The concentration of the acids has been varied as was done in the case of experiments with hydrous ferric oxide. Several acids like hydrochloric, acetic, propionic, butyric, etc., could not be used owing to their great peptising power, and hence the choice of acids used in this investigation is somewhat limited.

Wt. of Al_2O_3 used = 0.2670
Volume = 100 cc
Time = 20 hours, KCl = 0.05 mole per litre.

TABLE X
Adsorption of Oxalic Acid

Original conc. milli-equivalents	Conc. of solution after Adsorption	Adsorption per gram adsorbent
1.1320	0.6336	1.866
0.9517	0.4752	1.784
0.7615	0.3168	1.665
0.5711	0.1386	1.620
0.3808	0.0396	1.2770

TABLE XI
Adsorption of Sulphuric Acid

Original conc. milliequivalents	Conc. of solution after adsorption	Adsorption per grm adsorbent
1.1320	0.6535	1.7930
0.9902	0.5348	1.7060
0.7921	0.3565	1.6310
0.5940	0.1980	1.4840
0.39605	0.0793	1.1870

TABLE XII
Adsorption of Racemic Acid

1.1320	0.6237	1.9040
0.9802	0.4950	1.8180
0.7841	0.3366	1.6760
0.5882	0.1882	1.4980
0.3921	0.0396	1.3200

TABLE XIII
Adsorption of Malic Acid

1.1320	0.6735	1.7180
0.9219	0.4753	1.6730
0.7902	0.3566	1.6240
0.6582	0.2472	1.5390
0.5267	0.1584	1.3790

TABLE XIV
Adsorption of Citric Acid

Original conc. milliequivalents	Conc. of solution after adsorption	Adsorption per grm adsorbent
1.1320	0.5048	2.3490
0.9109	0.3268	2.1880
0.6831	0.1584	1.9650
0.4554	0.0594	1.4840
0.2277	0.0099	0.8158

TABLE XV
Comparative adsorption of some acids when the initial concentration is the same

Conc. of acid = 1.1320 milliequivalent per 100 cc.
Wt. of Al_2O_3 used = 0.2670 gr.

Acid	Adsorption per grm adsorbent.	Acid	Adsorption per grm adsorbent
Citric	2.3490	Malic	1.7180
Racemic	1.9040	Hippuric	1.2740
Oxalic	1.8660	Succinic	1.2740
Sulphuric	1.7930	Benzoic	0.7543

So far, the results obtained in the adsorption of acids by alumina has been given. It has however been shown that sodium arsenite is also highly adsorbed by alumina and the amount of adsorption expressed in terms of iodine is the same for both the arsenite and pure arsenious acid. In this connection the adsorption of some other salts and alkali has been investigated. In the case of salts like sodium phosphate, sodium citrate, etc., usually the negative ion is preferentially adsorbed when the solutions of these salts are shaken with freshly precipitated alumina. This change is noticeable by adding to

the solution some phenolphthalein when the pink colour is obtained. Quantitative results were however difficult to obtain owing to the smallness of the value of adsorption.

The amount of adsorption of alkali by alumina is however quite appreciable, and has been investigated in the usual way. In Table XVI, the results are shown. The amount of alumina is the same as used in the experiments with acids, and other conditions also remain the same.

TABLE XVI

Adsorption of Caustic Soda

Original conc. milliequivalents	Conc. of solution after adsorption	Adsorption per gram adsorbent
1.1320	0.7999	1.244
0.9909	0.8608	1.161
0.7921	0.4960	1.109
0.5940	0.3179	1.034
0.3960	0.1399	0.959

From these results it is obvious that the adsorption of alkali by alumina is fairly great, and in some cases comes to about 25 per cent of the total amount. Alumina, therefore, adsorbs not only acids, but also bases to a considerable extent.

Chemical Laboratory
Allahabad University

22

21

THE IONISATION OBTAINED BY BUBBLING AIR THROUGH VARIOUS SOLUTIONS

BY CHARLES R. PITTS

It is commonly known that, when air is bubbled through a liquid, electrical charges of both signs are carried along with it, one of which is in excess of the other in most cases. At the outset of this paper I would like to go over, in some degree, the historical background of the ionisation produced by bubbling air through liquids.

Lenard[1] investigated the well-known fact that there is something exceptional taking place in the phenomena of atmospheric electricity at the foot of a waterfall, when the water falls upon the rocks and breaks into a spray. The splashing of rain changes the atmospheric electrification; it electrifies the air negatively. Lord Kelvin[2] found that when air is bubbled through water there was a negative charge carried along with it; but when air was caused to bubble with great vigor the air carried along with it both positive and negative ions, though the latter were the more numerous; air treated in this way was found to discharge a body with a negative charge, though not so rapidly as one with a positive charge. He also found that with the addition of salts and acids to the water the effect was diminished, and in some cases the sign of the total electrification was reversed.

Kösters[3] found that while air is bubbled through pure water it was negatively charged, but with the addition of .007% of sulphuric acid to the water the air came through electrically neutral and with the addition of more acid the charge was positive.

De Broglie[4] varied the investigation by splashing or breaking up of the drops of water in air and called his experiment, "Ionisation by Bubbling" (*barbotage*). He showed that the intensity of ionisation obtained by the splashing of drops produced by forcing a liquid through an orifice on to a plane surface depended greatly on the diameter of the orifice. It was weak for capillary tubes and then passed to a maximum and again became weak for large diameters.

Among those who have investigated the ionisation produced by the bubbling of air through liquids are: Lord Kelvin, Maclean,[5] Kösters, MacTaggart[6], and de Broglie.

All these experiments show that the change in area of a liquid surface in contact with a gas gives rise to an electrification of the gas.

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[1] Wied. Ann., **46**, 584 (1892).
[2] Proc. Roy. Soc., **57**, 535 (1894); Phil. Trans., **191A**, 187 (1898).
[3] Wied. Ann., **69**, 12 (1899).
[4] Compt. rend., **145**, 172 (1907).
[5] Phil. Trans., **191A**, 187 (1898).
[6] Phil. Mag., (6) **27**, 297; **28**, 367 (1914).

It was shown by Holmgren[1] that when the surface of water was changing rapidly, for example, when ripples were travelling over the surface, or when two wet cloths are brought together and then suddenly pulled apart, electrification was produced, the negative in each case being in the air.

Evaporation of the liquid will not carry away a charge unless it is attended by agitation. It may be easily shown that if the vapor escaping from a charged surface of water carries with it any charge it must be very small. Many experimenters have failed to observe any loss from a liquid due to its evaporation. Pellat,[2] in his experiments on this subject made observations extending over an hour and then was able to detect only a very small loss from a large surface of water, and with a very sensitive apparatus.

It has long been recognized, largely on account of the properties of the capillary electrometer, and the electrical effects obtained with the bubbling of gases through liquids, that the surface of a solution, and the interfacial surfaces of a solution in contact with a metal or another solution might be the seat of an electrical segregation resembling a charged condenser. The condition of the formation and existence of these double layers have been investigated mathematically by Kleeman[3], and made the basis of a theory of the voltaic cell. The segregation of electricity arises, it might be pointed out, through the transition layer changing in density from one side to the other, and in which the ions of different signs therefore have different values for the coefficient of diffusion and mobility. This gives rise to a distribution of ions so that on passing from one side of this transition layer to the other, at first ions of one sign are in surplus, which increases and then decreases to zero, and which is followed by a surplus of ions of the other sign which also passes through a maximum. Thus in a solution the number of ions of one charge predominate in number over the ions of opposite charge near a metal surface or at the surface of the liquid.

Experiments to determine the electrical nature of the layer furthest from the surface have been carried out by Kleeman and the writer.[4] It is highly probable that this layer has something to do with the electrification produced by bubbling.

When the bubbles explode at the top of the liquid there is a certain decrease in the surface, which must be attended by some electrical rearrangement that might conceivably have an effect on the adjacent gas. Possibly absorbed air in the ionized condition in the layer is expelled.

In looking through the literature on the experiments by the above-named men in no place has there been found an extensive investigation including the common soluble salts. It was the intention in this investigation to cover the field more fully than heretofore; to determine the relative amount of ions of both signs and to determine the charge excess liberated when air is bubbled through every aqueous solution obtainable.

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[1] Societe physiographique de Lund, (1894).
[2] Compt. rend., **128**, 169 (1899).
[3] Phys. Rev., (2) **20**, 174 (1922).
[4] Kleeman and Pitts: J. Phys. Chem., **29**, 508 (1925).

The experiments were carried out by means of an apparatus shown diagrammatically in Fig. 1. A glass tube (4) about 6 cm. in diameter and 50 cm. long was clamped with its axis vertical in a stand. The lower end of this tube was closed by a stopper, through which passed a glass tube of about 15 mm in diameter, which had a force pump attached to its lower end. Over the upper end a common baby nipple (2) was tied to the glass tube. This nipple was pierced at a number of places by a thin sewing needle. Hence, when the tube (4) contained a solution and the pump was operated, small bubbles of air was formed on the surface of the rubber nipple and rose to the surface of the solution, the size of the bubbles depending on the pressure of the air from the pump. This pressure could be regulated at will by means of a suitable attachment.

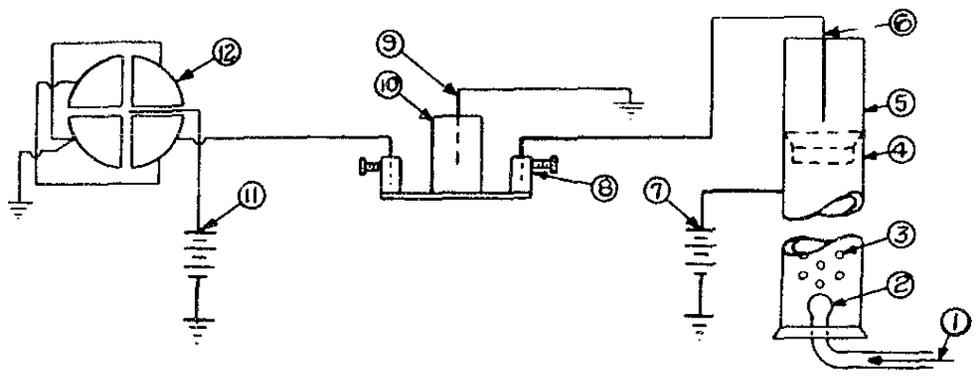


FIG. 1

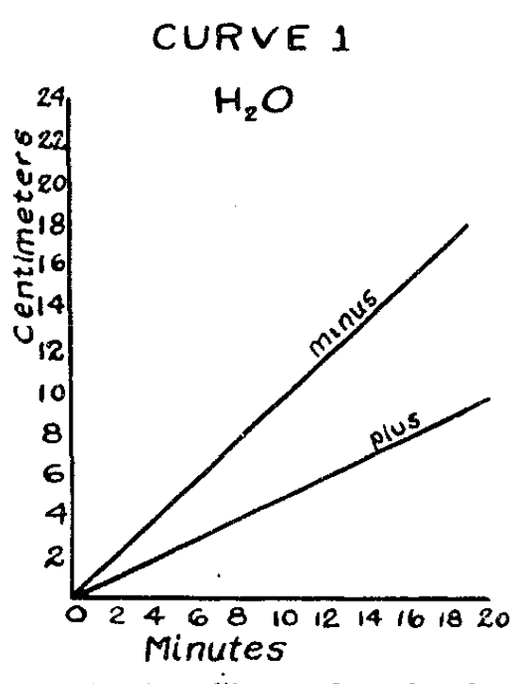
1) Direction of air from pump.
2) Baby nipple.
3) Solution bubbling.
4) Glass tube containing solution.
5) Copper cylinder.
6) Electrode.
7) Bank of B-batteries.
8) Copper terminal.
9) Grounding key.
10) Vessel containing $CaCl_2$.
11) Bank of B-batteries to needle of electrometer. (maintained +)
12) Quadrant electrometer.

This force pump was an electrically-driven blower and vacuum pump, the type used for producing a blast for the operation of blast lamps, and for use requiring moderate air pressure and vacuum. The outer casing of the blower is water-jacketed so that the heat developed during continuous use may be removed.

Resting on the top of the glass tube was a copper cylinder (5) which is about 20 centimeters long. Number (7) represents a bank of B-batteries of 180 volts connected through a reversing key to this copper cylinder (5). Number (6) represents an electrode, which was centrally located inside of the copper cylinder (5). This electrode was connected directly to a quadrant electrometer through the short-circuiting switch (9) or earthing key of special construction. A copper rod, having one end connected to earth and the other end dipped into a brass vessel containing a solution of calcium chloride, passes through an earthed metal tube. A conducting wire, which is attached to the quadrants of the electrometer, is attached to the earthing key by means of a terminal. On raising the rod (9) the quadrants are insulated, and, when bubbling is taking place, a current begins to flow from this electrode to the

electrometer. The key and its connections are enclosed in a metallic case and connected to ground to protect them from electrostatic disturbances. The key is raised and lowered by means of a string passing out of the metallic case over a pulley.

In making measurements of these ionisation currents, the electrometer and all of its connections were enclosed in metallic conductors connected to ground for shielding purposes. The wire leading to the electrometer was passed through a brass pipe supported at each end by ebonite plugs. All ground connections were to water pipes and great care was taken to insure good contact by soldering.



As stated above, when air is caused to bubble vigorously through distilled water, both positive and negative ions are liberated; but the negative ions are liberated in excess. In order to determine the relative number of positive and negative ions liberated the copper cylinder (5) was placed on the glass cylinder (4) and kept, when bubbling, at potential of plus or minus 180 volts by means of the reversing switch. When this copper cylinder is positive, it will attract the negative ions liberated and repel the postive ions liberated to the electrode and thus charge up the electro meter positively. On reversing the polarity of this copper cylinder it would attract the positive ions liberated and repel the negative ions liberated to the electrode, this giving the electrometer a minus charge.

In each case the natural leak was taken with the polarizing battery on but with no bubbling. The grounding key (9) was removed and the electrometer deflection was noted over a period of several minutes, the polarity of the copper cylinder was then reversed and the natural leak was taken corresponding to the opposite sign. This natural leak, in the majority of cases, was zero, and where it was appreciable it was subtracted from the deflection when bubbling.

In determining this excess of ions liberated I was not particularly interested in any quantitative measurements, but more in the relative number of positive and negative ions liberated when salts were added to distilled water. Thus distilled water was first bubbled over a period of 20 minutes (Curve 1) first measuring the amount of negative ions liberated, then by reversing the polarity of the cylinder (5) measuring the amount of positive ions liberated, over the same period of time, and with the same amount of bubbling, thus the relative number of ions liberated could be determined by comparing the deflections of the galvanometer.

Distilled water was tried several times and it was found that the number of negative ions liberated was approximately 2 to 1 over the number of positive ions liberated. This was checked several times and this result was obtained each time within the range of experimental error.

Curve 1 shows the relative amounts of positive and negative ions liberated with time when air is bubbled through distilled water. The ordinates represent the scale deflections in centimeters and the abscissae represent the time of bubbling in minutes. The upper line represents the deflection when the electrometer is being charged negatively and the lower line represents the deflection when the electrometer is being charged positively. Thus the ratio +/− can be determined by dividing the positive deflection over any period of time by its corresponding negative deflection. Both of these lines show that the amount of positive and negative ions liberated under these conditions is practically a straight line relation. It has been stated in the first part of this paper that negative ions are liberated in excess, and these curves show conclusively that this is correct.

Table I shows the ratio of the number of positive ions to the number of negative liberated in the case of salt solutions, namely, +/−. The deflection

TABLE I

Table of Ratios of Positive and Negative Ionization obtained by bubbling Air through Solutions

Substance	Concen. (Mol. fr.)	Ratio of +/−
Sulphates		
$CuSO_4$	2%	1.28
$CuSO_4$	2%	1.32
$CuSO_4$	2%	1.39
$CuSO_4$	2%	1.50
$Fe(SO_4)_3$	2%	.87
$FeSO_4$	2%	.95
$NiSO_4$	2%	.86
$NiSO_4.6\ H_2O$	2%	.77
$CdSO_4$	2%	.74
$MgSO_4$	3.34%	.615
Na_2SO_4	2%	.74
$MgSO_4$	2%	.96
$MgSO_4.7\ H_2O$	2%	.68
$ZnSO_4$	2%	.65
Al_2KSO_4	2%	.95
Al_2KSO_4	2%	.95
$Al_2(SO_4)_3$	2%	.77
Oxalates		
FeC_2O_4	2%	.53
$Fe_2(C_2O_4)_3$	2%	.69

TABLE I (Continued)

Table of Ratios of Positive and Negative Ionization obtained by Bubbling Air through Solutions

Substance	Concen. (Mol. fr.)	Ratio of +/−
	Fluorides	
NH_4F	2%	.71
	Iodides	
FeI_2	2%	1.35
CdI_2	2%	3.0
KI	2%	.98
KI	13.1%	1.85
NaI*	2%	
MgI_2	2%	1.55
BaI_2	2%	.81
NH_4I	2%	.67
	Carbonates	
K_2CO_3	2%	.68
	Chromates	
K_2CrO_4	15.1%	4.5
K_2CrO_4	2%	.98
Na_2CrO_4	2%	.88
	Permanganates	
$KMnO_4$	2%	1.05
	Hydroxides	
KOH	2%	.83
	Phosphates	
Na_3PO_4	2%	.83
$NH_4H_2PO_4$	2%	.81
	Nitrates	
$Cu(NO_3)_2$	2%	1.075
$Fe_2(NO_3)_3$	2%	1.10
$Ni(NO_3)_2$	2%	1.071
$Cd(NO_3)_2$	2%	1.027
$NaNO_3$	2%	.92
$Mg(NO_3)_2$	10%	1.35
$Mg(NO_3)_2$	2%	
$Ba(NO_3)_2$	4%	3.0
$Ba(NO_3)_2$	2%	1.06
NH_4NO_3	2%	1.05
$Zn(NO_3)_2$	2%	.78
$Al(NO_3)_3$	2%	.83

* No excess

TABLE I (Continued)

Table of Ratios of Positive and Negative Ionization obtained by Bubbling Air through Solutions

Substance	Concen. (Mol. fr.)	Ratio of +/−
	Acetates	
$Cu(C_2H_3O_2)_2$	1%	1.7
$Cu(C_2H_3O_2)_2$	2%	.94
$Cd(C_2H_3O_2)_2$	2%	1.23
$K(C_2H_3O_2)$	2%	.81
$Na(C_2H_3O_2)$	2%	1.11
$NH_4(C_2H_3O_2)$	2%	.76
$Mn(C_2H_3O_2)$	2%	.79
	Chlorides	
$CuCl_2$	2%	1.10
$FeCl_2$	2%	1.17
$FeCl_2$	2%	1.15
$CdCl_2$	7%	1.28
$CdCl_2$	2%	.95
KCl	2%	.89
NaCl	2%	1.08
HCl	2%	.94
HCl	2%	.90
$MgCl_2$	2%	1.17
$BaCl_2$**	2%	1.14
$BaCl_2$**	2%	.91
$BaCl_2$**	2%	.84
NH_4Cl	2%	1.11
$ZnCl_2$*	2%	
$AlCl_3$	2%	1.58
	Bromides	
$CuBr_2$	2%	1.05
$FeBr_3$	2%	1.02
$FeBr_2$	4.61%	1.14
$FeBr_2$	2%	1.05
$NiBr_2$	2%	1.10
$CdBr_2$	7%	.82
$CdBr_2$	2%	1.06
KBr	2%	.98
NaBr	2%	.84
NH_4Br	2%	.75

* No excess
** Different solutions

was noted over a period of two minutes, then the polarity of the copper cylinder (5) was reversed and the deflection corresponding to the opposite sign over the same length of time and with the same amount of bubbling was noted. This was done four times for each sign and the ratio of the means was taken. There is considerable error in an experiment of this kind, but these results agree within 10%. In the case of each solution tried the ratio of the +/− is increased from what was obtained with distilled water.

Table II shows the ratio of the number of positive ions liberated to the number of negative ions liberated, namely +/−, when air is bubbled through these solutions. The deflection was noted over a period of 10 minutes instead of 2 minutes as before, then the polarity of the copper cylinder was

TABLE II

Table of Ratios of Positive and Negative Ionization obtained by bubbling Air through Solutions

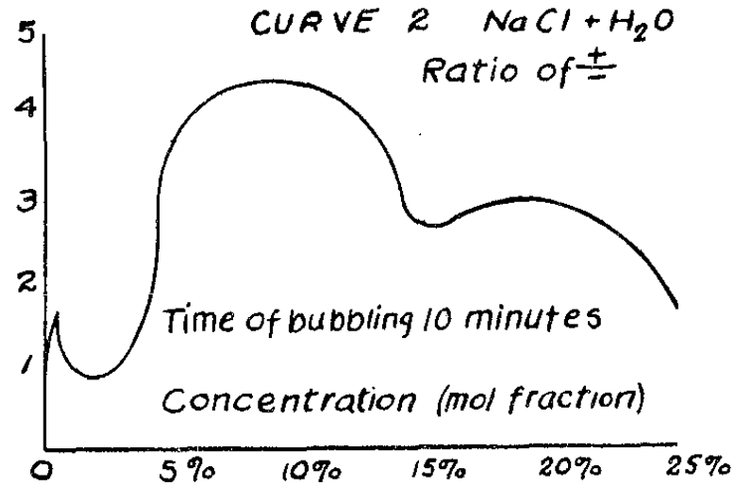
Substance	Concen. (Mol. fr.)	Ratio of +/−
$Cu(C_2H_3O_2).H_2O$	1%	1.71
$CuSO_4$	2%	1.29
$Mg(NO_3)_2$	10%	1.35
$MgSO_4$	3.34%	1.57
$FeBr_2.6\ H_2O$	4.6%	1.09
$Fe\ Cl_2.4H_2O$	2%	1.77
$CdBr_2$	2%	1.85
$CdBr_2$	7%	.82
$CdCl_2$	7%	1.28
KI	13.2%	1.85
K_2CrO_4	15%	4.51
$Cu(C_2H_3O_2).H_2O$	1%	1.71
$CuSO_4$	2%	1.29
$Ba(NO_3)_2$	4%	3.00
$Ba(NO_3)_2$	2%	1.42
$Mg(NO_3)_2$	10%	1.35
$MgSO_4$	3.34%	1.57
$FeBr_2.6\ H_2O$	4.6%	1.09
$Fe\ Cl_2.4H_2O$	2%	1.77
$CdBr_2$	2%	1.85
$CdBr_2$	7%	.82
$CdCl_2$	7%	1.28
KI	13.2%	1.85
K_2CrO_4	15%	4.51

Note: The above ratios (+/−) were obtained for bubbling over a period of 10 minutes.

reversed and the deflection corresponding to the opposite sign over the same length of time and with the same amount of bubbling was noted.

This ratio seems to depend to a slight extent, upon the time of bubbling as will be found on comparing the ratio +/− for solutions common to the Tables I and II. In most cases it increased but it was difficult to repeat these values because it probably depends upon the amount of absorbed air. If it does depend upon the amount of absorbed air, it would thus depend upon the previous treatment of the solution.

The ratio +/− depends on the concentration. The effect of concentration in the case of aqueous solutions of Na Cl was accordingly studied.



CURVE NO. 2

Concentration (Mol fraction)	Ratio of +/−
0%	·433
¼%	1.56
½%	1.16
1%	·97
3%	.88
5%	3.68
10%	4.46
15%	2.64
20%	2.93
25%	1.67

Note: The above ratios (+/−) were obtained for bubbling over a period of 10 minutes.

In studying the relative amounts of positive and negative ions liberated with concentration (mol fraction) of solution the following concentrations of NaCl and distilled water were used: 1/4%, 1/2%, 1%, 3%, 5%, 10%, 15%, 20%, and 25%. On Curve 2 the ordinates are the ratios of +/− and the abscissae are the concentrations of the solutions. At zero concentration or distilled water the minus is liberated in excess thus the ratio resulting in a decimal, but with the addition of more salt the ratio becomes larger, showing that the positive are now liberated in excess, and at higher concentrations the ratio steadily decreases thus showing that the minus are again being liberated in excess. Some important deductions can be made from this curve, namely,

by tracing along this curve we can find points where it crosses the line where the ratio $+/-$ equal 1, determining the amount of salt which is necessary to make an aqueous NaCl solution electrically neutral. This is similar to the work which Kösters did, as already referred to in bubbling sulphuric acid.

It may be noted from Curve 2 that for lower concentrations (¼%, ½%, 1% and 3%) the value of $+/-$ does not vary very much. Beyond the 3% solution its value increases rapidly to a maximum and for high concentration decreases and becomes nearly unity again. Thus we are led to believe that the ratio $+/-$ in the case of an aqueous solution of NaCl in general decreases, increases, and then decreases.

It is likely that the other solutions show a similar behaviour with change in concentration. A line of further and important research is thus suggested.

I desire to express my thanks to Dr. Kleeman for suggesting this research and for helpful suggestions in carrying it out. I wish to express my appreciation to the General Electric Company and to the Chemistry Department at Union College for their assistance in obtaining chemicals used in this investigation.

Physics Department
Union College

THE POSITIONS OF THE K-ABSORPTION LIMITS OF VANADIUM IN VARIOUS OF ITS COMPOUNDS

BY STERLING B. HENDRICKS AND RALPH W. G. WYCKOFF

Introduction

Recent experiments have shown that the positions of the X-ray absorption limits of an element depend upon the state of its chemical combination. Early measurements of this character indicated[1] that the K-absorption limit from white phosphorus occurs at a slightly different wave length from the limit for red phosphorus. From subsequent observations,[2] for the most part upon compounds of phosphorus, chlorine and sulfur, it is clear that the valence of an element is an essential factor in determining shifts in its absorption edge. Existing data are nevertheless sufficient to show that other influences, not thoroughly evaluated, have important bearings upon these phenomena. The results of this paper, upon compounds of vanadium, are the first of a series of absorption measurements which it is hoped will eventually provide data necessary for an understanding of the phenomena of absorption. Since they appear to form some sort of a measure of the effects of chemical changes upon atomic structure, their systemmatic investigation is of both chemical and physical interest. The absorption edges of vanadium compounds are comparatively easy to measure because, though this K-absorption limit falls within a region where the magnitude of the wave length shift far exceeds the error involved in its measurement, such X-rays are not so soft that the experimental manipulation becomes difficult.

The Method of Experimentation and the Accuracy of the Results

For wave lengths shorter than 1.0Å shifts in absorption limits are of the same order of magnitude as the errors inherent in the most accurate measurements of X-ray wave lengths. Even though they are increasingly significant at longer wave lengths, their careful study requires that methods of precision spectrometry always be employed.

A Siegbahn vacuum spectrograph[3] of the usual type has been employed. In this instrument the crystal-to-plate distance is approximately equal to the crystal-to-slit distance. All photographs have therefore been made with a stationary crystal. The slit, 0.1mm. wide, was covered with a thin film of collodion. The measured spectra were either second or fourth order reflections from (100) of calcite. The spacing of this second order reflection[4] has been taken to be 3029.04 X. U.

[1] J. Bergengren: Z. Physik, 3, 247 (1920); Compt. rend., **171**, 624 (1920).

[2] A. E. Lindh: Z. Physik, **6**, 303 (1921); Dissertation, Lund (1923); Compt. rend., **172**. 1175 (1921); **175**, 25 (1922); Ark. Mat. Astr. Fys., **18**, 12 (1924); Z. Physik, **31**, 210 (1925); D. Coster: Z. Physik., **25**, 83 (1924 ; O. Stelling: Z. anorg. Chem., **131**, 48 (1923); Z. phys. Chem., **117**, 161, 175 (1925 ; H. Fricke: Phys. Rev; (2) **16**, 202 (1920); G. A. Lindsay and G. D. Van Dyke; Phys. Rev. (2) **28**, 613 (1926).

[3] M. Siegbahn: "The Spectroscopy of X-rays," Chap. III (1925).

[4] Siegbahn: ibid., p. 84.

Two entirely different sets of experiments were carried out, using different targets as sources of X-rays and different calcite crystals as gratings. In the first group, upon V_2O_5 and NH_4VO_3, the water-cooled metal tube had a platinum anticathode. The crystal-to-plate distance for these experiments was accurately determined by measuring, upon a series of second order Cu-K spectra, the separation of the lines Cu-Kα_2 and Cu-Kβ_1. The accepted wave lengths[1] have been used for these and all other emission lines. Wave length measurements upon the vanadium absorption limits were then obtained from separations measured between these edges and the fourth order Pt-Lβ_1 line always occurring upon the plates. In a second and more numerous group of experiments, upon V_2O_5 and NH_4VO_3 as well as upon all the other vanadium compounds subsequently to be mentioned, a tube with a thorium target was employed. Standard emission lines of a suitable wave length arose from placing a small quantity of metallic chromium upon this anticathode. The crystal-to-plate distance was deduced from a series of measured separations between Cr-Kα_2 and Cr-Kβ_1. The standard emission lines from which the wave lengths of the absorption edges were directly calculated were either Cr-Kα_2 or Cr-Kα_3. In all these experiments the X-ray tube was operated at a peak voltage of from 8000V to 10000V with a current of 30-35MA. Two hour exposures furnished good photographs.

The compound to be examined was prepared by grinding a small weighed quantity with a known volume of celluloid dissolved in amyl acetate. This suspension was poured upon a given area of glass plate and allowed to harden. The resulting film, after being blackened with india ink, was placed between the slit and the crystal. Liquids were mounted in the same manner. Certain compounds of vanadium, however, react with the amyl acetate-celluloid solution. In such cases another method was used. The compound was suspended in melted paraffin and allowed to cool. Thin sections were then removed with a razor. A new specimen was always used for each photograph that was made. The samples for the vanadium compounds studied contained from 2 to 10 mgs. per. sq. cm. and were from 0.01 to 0.1 mm. in thickness.

The plates were measured on a comparator having a screw accurate to 0.001 mm. The details of interest on the plates could be measured to about 0.01 mm. Both visual and photometric observations have been carried out. Under existing experimental conditions the visual measurements (using magnification of ca 3×) proved to yield the more significant and reproducible results. They have therefore served as the basis for all of the data recorded in this paper.

Some of the present measurements are lower than previous ones[2] on salts of vanadium by an amount which exceeds the probable error. (See Table I). In such instances both Pt-Lβ_1 (2) and Cr-Kα_3 were used as reference lines. The former of these is on the short wave length, the latter on the long wave length, side of the edge. The fact that both sets of the present results agree within

[1] Siegbahn: op. cit.

[2] D. Coster: op. cit.; A. E. Lindh: op. cit.

TABLE I
K-Absorption Edges of Vanadium Compounds

Compound.	Wave Length according to *Lindh*	*Present results*
V	2263.2 X. U.	2263.2 X. U.
V_2O_5	2257.4	2256.8
NH_4VO_3	2257.3	2256.9

the limit of accuracy indicates that all of the data of this paper are precisely comparable amongst themselves. Since the shape of a photometered curve is a function of such factors as the width of the photometer slit, it is possible that the divergence of the earlier results may arise from the selection of different features of the absorption.

In both the emission photographs made for purposes of standardization and in the absorption photographs, each plate was measured five times in either two or three separate positions. The final result is thus an average of from ten to fifteen distinct measurements. Representative data from a typical photograph are recorded in Table II. Four separate photographs were usually made from each compound.

TABLE II
Measurements upon a Typical Photograph (of K_3VO_4)

	First Setting		Second Setting	
	#1	#2	#1	#2
Position of α_2 line	154.715mm.	154.695	154.760	154.770
Separation from α_2 of α_3	1.035mm.	1.040	1.040	1.040
1st edge of white line	1.687	1.728	1.720	1.718
2nd edge of white line	1.830	1.863	1.848	1.858
Absorption edge	2.035	2.045	2.040	2.032

Preparation of the Compounds

Although no great effort was made to prepare pure compounds, care was taken adequately to identify the preparations used. Criteria for this purpose were either a determination of the vanadium content or else some characteristic reactions and physical properties. Attention was at all times given to the possibility of decomposition of the compound under the action of the X-rays.

All analyses were made through SO_2 reductions of the vanadium compound in H_2SO_4 solution to the vanadyl state. The excess SO_2 was removed by CO_2 and the hot solution titrated with $KMnO_4$(ca N/20). Objectionable acids were first removed by evaporating with H_2SO_4. Lower valence compounds were at the outset oxidized with HNO_3 or H_2O_2—the excess of oxidizing agent being later destroyed.

Absorption measurements have been made upon the following preparations.

V_2O_5 (a) Commercial (Red). 49.80% V. (calc. for V_2O_5, V = 56.04%) (b) Yellow (Kahlbaum product).

V_2O_4, V_2O_3 Measurements were made upon samples supplied by Prof. L. M. Dennis of Cornell University.

$VO-V(OH)_2$[1] Brownish purple $V(OH)_2$, obtained by adding an excess of NH_4OH to a solution of a vanadous salt, was dried in a current of oxygen-free CO_2 and later heated to a red heat. This material showed the characteristic reactions of vanadous salts—it decomposed acids with an evolution of hydrogen, thus furnishing an acid solution which had the green color of a vanadic salt. Analysis gave the following result: 64.0% V (calc. for VO 76.11% V; calc. for $V(OH)_2$ 60.00% V).

V Measurements were carried out upon a chemically pure product supplied by Dr. Jordan of the Bureau of Standards.

K_3VO_4 A melt[2] of one mol of V_2O_5 and three mols of anhydrous K_2CO_3 was held liquid at 1000°C for several hours. The product contained a slight excess of carbonate.

Na_3VO_4 The method of preparation resembled that used for K_3VO_4. One mol of V_2O_5 was fused with three mols of $Na_2CO_3.H_2O$.

NH_4VO_3 Kahlbaum. 43.48% V (calc. for NH_4VO_3, V 43.59%).

$K_4V_2O_7$ The method of preparation was the same as that used for K_3VO_4 except that one mol of V_2O_5 was fused with two mols of K_2CO_3. In these fusions, a large excess of either of the reacting substances was required to be absent.

Na_3VS_3O By passing[3] dry H_2S over Na_3VO_4 at a red heat, Na_3VS_3O was obtained as a red brown crystalline powder melting without change to a purple liquid.

V_2S_3 Commercial[4] V_2O_5 (containing 49.80% V), heated to redness in a current of CS_2 gave V_2S_3 as a graphitic black powder. Analysis: 46.40% V (calc. for V_2S_3, 51.51% V).

V_2S_5 V_2S_3 and a large excess[5] of sulfur were heated to 500°C in a closed tube.

$VOCl_3$ V_2O_5 mixed[6] with P_2O_5 was treated at 80°C with dry HCl. The resulting clear yellowish-red liquid was redistilled without exposure to the air. This $VOCl_3$ forms with amyl acetate-celluloid a dark red solution. It also dissolves in paraffin giving it a similar dark red color. Both preparations yielded the same edge.

VOCl Employing a stream of dry hydrogen, freshly[7] prepared $VOCl_3$ was distilled into a tube having a small portion of its length heated to bright redness. Light brown VOCl deposited beyond this heated portion.

VCl_4, VCl_3 Dry chlorine was passed over well powdered ferro-vanadium with the formation of VCl_3, $FeCl_3$, and VCl_4. The more volatile VCl_4 was separated by several distillations as a dark reddish brown liquid. Purple

[1] Roscoe: Ann. Pharm. Suppl., **6**, 454 (1868); Gmelin-Kraut: Handbuch anorg. Chem., **3**, II, 74.

[2] Rammelsberg: Ann. Physik, (2) **20**, 928 (1883).

[3] J. Locke: Am. Chem. Jour., **20**, 373 (1898).

[4] W. E. Kay: J. Chem. Soc., **37**, 373 (1898).

[5] W. E. Kay: op. cit.

[6] F. Ephraim: Z. anorg. Chem., **35**, 66 (1903).

[7] Roscoe: Ann. Pharm. Suppl., **6**, 114 (1868).

crystals of VCl_3 were deposited in the VCl_4 containers. By following this procedure contamination by oxychlorides is prevented. Both halides were mounted in melted paraffin. Unless the temperature is maintained as low as possible, VCl_4 reacts with the paraffin giving copious fumes of HCl.

NH_4VO_4 A saturated[1] aqueous H_2O_2 solution of NH_4VO_3 was treated with alcohol. The yellow powder precipitating out was washed with ether and dried in air. Analysis: 37.27% V (calc. for NH_4VO_3, 38.34% V). It is probable that NH_4VO_4 decomposed under the conditions of these experiments.

Experimental Results

Data from the vanadium compounds examined are listed in Table III. In agreement with previous results some of the plates showed near the absorption edge a white line, similar in appearance to a reversed emission line. Because its long wave length edge coincides with the absorption edge of metallic vanadium, this white line has been supposed[2] to arise from reduction to the metal of vanadium in the samples. It seems hard to reconcile this explanation with the relative chemical stabilities of the vanadium compounds which have been investigated. The experiments recorded in this paper do not satisfactorily establish the source of this phenomenon. It is therefore felt that its more detailed discussion may profitably await further experimental results.

The effect of valence upon the absorption edges of the compounds of Table III is made evident by Table IV. Absorption edges from pentavalent vanadium have the lowest wave lengths. Taken as a whole the compounds with lower valence yield absorption edges which are at longer wave lengths the lower the valence. Nevertheless compounds of a single valence type show pronounced variations among themselves and it sometimes happens that compounds of one valence group overlap those of adjacent groups. Chlorides and oxychlorides give longer wave length edges than the corresponding sulfides and oxides. If compounds of the same chemical sort are compared (Table V), the increase of wave length with decrease in valence is more regular.

Comparisons between the pentavalent compounds of vanadium bring out several interesting facts (Table VI). The two binary compounds V_2O_5 and V_2S_5 give much shorter edges than any others except NH_4VO_3. Pyro- and ortho-vanadates are similar but their edges differ markedly from that of the meta-vanadate that was studied. The edge for Na_3VO_4 is appreciably different from that for the corresponding potassium salt. It is of interest to observe that the substitution of sulfur for oxygen in these compounds produces only slight absorption edge changes.

It is easy to understand qualitatively why a shift occurs in the X-ray absorption edge when the chemical valence of an atom changes. Apparently conclusive reasons exist for the belief that an increase in positive valence corresponds to a decrease in the number of electrons surrounding an atom.

[1] A. Scheurer: Z. anorg. Chem., **16**, 294 (1898).

[2] K. Chamberlain: Phys. Rev., (2) **26**, 525 (1925); A. E. Lindh: op. cit.

TABLE III

K-Absorption Edge Measurements upon Compounds of Vanadium

Compound	Reference line	White Line: Long Wave Length Edge[1] mm.	X.U.	White Line: Short Wave Length Edge[2] mm.	X.U.	Absorption Edge mm.	X.U.	Δλ	V/R	ΔV in volts
V_2O_5	$PtL\beta_1(2)$					1.48	2256.6(5)	6.6	403.83	15.9
	$CrK\alpha_3$	0.70	2262.9(2)	0.85	2260.6(2)	1.11	2256.8(2)	6.4	403.79	15.4
V_2O_4	$CrK\alpha_2$					1.96	2259.0(2)	4.2	403.40	10.1
	$CrK\alpha_3$					1.00	2258.8(3)	4.4	403.44	10.6
V_2O_3	$CrK\alpha_3$					0.93	2259.5(4)	3.7	403.31	8.9
	$CrK\alpha_2$					1.98	2259.2(3)	4.0	403.36	9.7
VO	$CrK\alpha_2$					1.91	2260.1(4)[3]	3.1	403.20	7.5
V	$CrK\alpha_2$					1.71	2263.2(3)	0.0	402.65	0.0
K_3VO_4	$CrK\alpha_3$	0.68	2263.2(4)	0.82	2261.1(4)	1.00	2258.3(4)	4.9	403.53	11.8
	$CrK\alpha_2$	1.72	2263.1(4)	1.86	2261.0(4)	2.04	2258.2(4)	5.0	403.54	12.1
Na_3VO_4	$CrK\alpha_2$	1.72	2263.1(1)			2.09	2257.4(3)	5.8	403.69	14.0

[1] Average value 2263.1. Maximum deviation .3. Mean deviation .14.
[2] Average value 2260.9. Maximum deviation .6. Mean deviation .26.
[3] Contains $V(OH)_2$ and perhaps V_2O_3.

TABLE III (Continued)

NH_4VO_3	PtLβ_1(2)	1.89	2262.6(5)	1.72	2260.3(5)	1.47	2256.6(5)	6.6	403.83	15.9
	CrKα_2					2.13	2256.9(2)	6.3	403.78	15.2
$K_4V_2O_7$	CrKα_3	0.68	2263.2(3)	0.82	2261.0(3)	1.01	2258.2(4)	5.0		
	CrKα_2	1.70	2263.4(3)	1.85	2261.1(3)	2.04	2258.2(3)	5.0	403.54	12.1
Na_3VS_3O	CrKα_2					2.05	2258.0(3)	5.2	403.58	12.5
V_2S_5	CrKα_2					2.16	2256.4(3)	6.8	403.86	16.4
V_2S_3	CrKα_2					1.93	2260.0(3)	3.2		
	CrKα_3					0.89	2260.0(3)	3.2	403.22	7.7
$VOCl_3$	CrKα_2					2.03	2258.4(3)	4.8	403.51	11.6
VOCl	CrKα_2					1.96	2259.4(3)	3.8	403.33	9.2
VCl_4	CrKα_2					1.93	2259.9(4)[4]	3.3	403.24	8.0
VCl_3	CrKα_2					1.86	2260.9(2)	2.7	403.09	6.5
NH_4VO_4	CrKα_2	1.72	2263.0(3)	1.84	2261.2(2)	2.12	2257.1(4)		403.74	

decomposed.

[4] Mounted in paraffin.

Note: The parenthesized numbers of columns 4, 6 and 8 indicate the number of photographs upon which the corresponding results are based.

TABLE IV

The Absorption Edges of Vanadium Compounds arranged according to their Valences

Compound	Edge	Compound	Edge	Compound	Edge	Compound	Edge	Compound	Edge
V_2O_5	2256.8X.U.	V_2O_4	2259.0	V_2O_3	2259.2	VO	2260.1	V	2263.2
V_2S_5	2256.4	VCl_4	2259.9	V_2S_3	2260.0				
$VOCl_3$	2258.4			VOCl	2259.4				
K_3VO_4	2258.2			VCl_3	2260.9				
$K_4V_2O_7$	2258.2								
Na_3VO_4	2257.4								
Na_3VS_3O	2258.0								
NH_4VO_3	2256.9								

TABLE V

Absorption Edges of Vanadium Compounds arranged according to Types

Oxides	X. U.	Sulfides	X.U.	Chlorides	X. U.	Oxychlorides	X. U.
V_2O_5	2256.8	V_2S_5	2256.4	VCl_4	2259.9	$VOCl_3$	2258.4
V_2O_4	2259.0	V_2S_3	2260.0	VCl_3	2260.9	VOCl	2259.4
V_2O_3	2259.2						
VO	2260.1						
V	2263.2						

TABLE VI

Absorption Edges of Compounds of Pentavalent Vanadium

Compound	X.U.	Compound	X. U.
V_2O_5	2256.8	K_3VO_4	2258.2
V_2S_5	2256.4	$K_4V_2O_7$	2258.2
		Na_3VO_4	2257.4
		Na_3VS_3O	2258.0
		NH_4VO_3	2256.9

With this decrease in the number of associated electrons the intensity of bonding of any electron by the nucleus becomes greater. It is a consequence of such an increase in the "effective nuclear charge" that more energy will be required to eject an electron from any energy level in the atom. In terms of such pictures as can now be formed concerning the mechanism underlying the production of X-ray absorption limits, this would result in a shift of these limits towards shorter wave lengths. Though a qualitative explanation of this character may well be correct, its quantitative aspects must be much more complex.

Probably the most important problem now facing valence theory is the question of the existence of shared electrons. Measurements of absorption edges furnish an experimental way of evaluating the effect of chemical combination upon atomic structure. As such they may perhaps be made to tell whether, as a result of the chemical union between a strongly electropositive and a strongly electronegative atom, electrons are completely transferred from one atom to the other. The variations already found in edges from atoms in the same valence state conclusively show that the positions of these edges depend upon other factors than the numerical value of the valence. Among these influences the following might be expected to be important:

(1) The group opposite in sign to that bearing the atom studied, e.g. Na_3VO_4, K_3VO_4; KCl, NaCl.

(2) Different kinds of atoms forming the group which contains the atom, e.g. Na_3VO_4, Na_3VS_3O, Na_3VS_4, etc.

(3) The numbers of atoms immediately associated with the atom under investigation, e.g. $NaVO_3$ and Na_3VO_4.

(4) The physical state of the compound.

(5) Polymorphism, e.g. red and white phosphorus.

(6) The crystal structure of the compound.
(7) Temperature.

An evaluation of these factors is obviously a preliminary to any satisfactory explanation of absorption edges but many additional experimental data are needed to achieve such a result.

Conclusions

Accurate measurements have been made of the K X-ray absorption limits of vanadium in several of its compounds. The nature of the variations observed in these limits are mentioned and possible factors determining them are briefly discussed.

Geophysical Laboratory,
December, 1926.

THE ZONE PATTERN FORMED BY SILVER DICHROMATE IN SOLID GELATINE GEL

BY E. RAYMOND RIEGEL AND MELVIN C. REINHARD

Introduction: In the course of further studies of the zone pattern formed by colored salts in solid gels[1], it was found possible to obtain the pattern, free from lines, with silver dichromate, the classical example of rhythmic band formation. The gelatine must be previously washed free of the impurities (chlorides) which form a white salt with silver nitrate. It was found that the chloride impurity in commercial gelatine gives itself with silver nitrate a deposit which forms the zone pattern also. The present work establishes that the substructure due to the impurity must be present if the red bands of the dichromate are to form. This conclusion had been reached before, but the evidence was less definite than in the present case. The previous work is fully reviewed further on. The existence of the substructure, that is the fine lines formed by the white silver salt in commercial gelatine, has been observed several times before; these observations are presented briefly. The previous studies have been either with flat glass plates covered with the gelatine, or in test tubes; and the silver solution has usually been extremely concentrated, (25%); whereas our work is done chiefly with cakes submerged in weak silver solution (1%), and with the soft slices cut from such cakes. The observations of the zone patterns are entirely new. Some experiments relating to the effect of sodium chloride addition on the penetration of the silver salt into the gel were also made (tubes).

Washing the Gelatine: On placing silver nitrate solution over a 4% commercial gelatine gel containing potassium dichromate, the red bands which form are preceded by a white haze, and when the action ceases, the haze extends well beyond the red bands. By washing the gelatine, the impurity causing the haze (sodium or calcium chloride) may be removed; in such a washed gelatine the red bands do not form, but merely an unbroken red zone with no haze detectable (test-tubes); the non-formation of haze or of the red bands is a delicate test of the thoroughness of the washing. This may be done in plain distilled water; 50 grams of commercial gelatine are placed in 4 liters of cold water and left 12 hours in contact with it, with occasional shaking; after that time the water is poured off and a fresh volume added. This is repeated twice more. The gelatine is then poured onto a large Buchner filter and freely washed for 1 hour.

Procedure for the Zone Pattern: A 4% solution of the washed gelatine, to which 0.1 gram of potassium dichromate is added for each 100 cc of solution, is allowed to solidify over night in the ice chest. The solid gel is cut into cubes of 3 to 4 cm at the side, and these are submerged in 1% silver nitrate solution for periods of varying lengths, but usually of 4 hours. On removal, a vertical

[1] Riegel and Widgoff: J. Phys. Chem., 29, 872 (1925).

slice 3 mm thick is cut from the center of the cake; it is found that the inner portion of the gelatine is clear, and that the cleared zone extends to the corners; the deposit is unbroken by lines; no white haze can be found. Two such slices are shown as B in the photograph below.

On adding a small amount of sodium chloride to the washed gelatine solution, and otherwise proceeding exactly as above, the red lines of the silver dichromate reappear, also the white haze. In Fig. 1, C represents such a slice from washed gelatine with sodium chloride addition, while A is the original commercial gelatine (unwashed) for comparison.

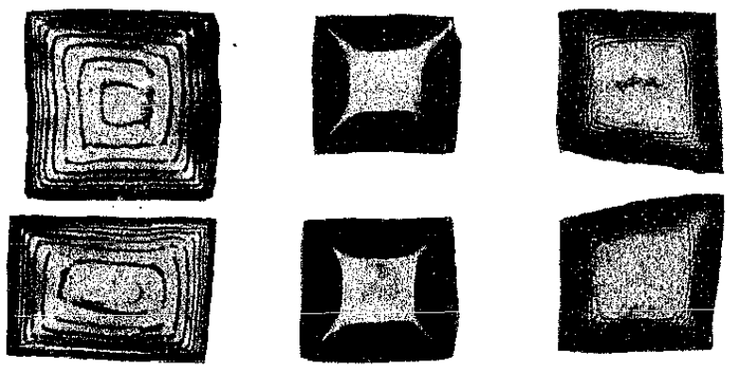


FIG. 1

The zone pattern formed by silver dichromate deposited in gelatine; A, original gelatine, showing bands; B, washed gelatine, free from lines, and showing the zone pattern; C, washed gelatine with added sodium chloride, showing the reappearance of the bands.

Examination of C established that the white haze had the fine line structure, although very faint.

Effect of Various Amounts of Sodium Chloride: The addition of sodium chloride to the washed gelatine, followed by the usual procedure, did not always result in the reappearance of the red bands, because the concentration of salts in the gel need not be very high to equal that of the outer salt, 1% $AgNO_3$, and prevent the formation of any silver dichromate. The decrease in penetration is well shown in the photograph below of 5 test tubes whose gels contained various amounts of NaCl. Each tube contained 10 cc of a 4% washed gelatine solution, to which 0.01 gram potassium dichromate had also been added; the amounts of NaCl were: a, 0.0015 gram; b, 0.003; c, 0.009; d, 0.018; and e, 0.03. The 5 gels were overlaid at the same moment with 10 cc of 1% silver nitrate, placed in the ice chest for 20 hours and photographed, Fig. 2. The penetration in *a* is three times deeper than in *e*, which has 20 times as much NaCl. No rings form in *d* nor in *e*; for good ring formation, with a 1% silver nitrate solution, the concentration of NaCl should be below 0.1%. An amount as small as 0.001% NaCl still gives rise to a red band. A deep penetration in *e* was not likely, for the amount of salt added to the amount of dichromate required almost all of the silver nitrate in the solution, so that the osmotic pressure in the gel would about equal that in the solution.

The deposit in *e* had some red silver salt when photographed; after 8 days, the deposit was snow white; the solution above the gel had turned yellow, while the other tubes still had colorless solution. The chlorine ion travels

to the reaction zone with great rapidity; some of the dichromate ions also move up however, as indicated by the fading of the gelatine just below the deposit, which fading may be observed in Fig. 2. On standing several days, the residual chloride ions move to the reaction zone and displace the dichromate ion in the more soluble silver dichromate; the second product of this displacement reaction, sodium dichromate, passes into the solution (now nearly water) above the gel, tinting it yellow.

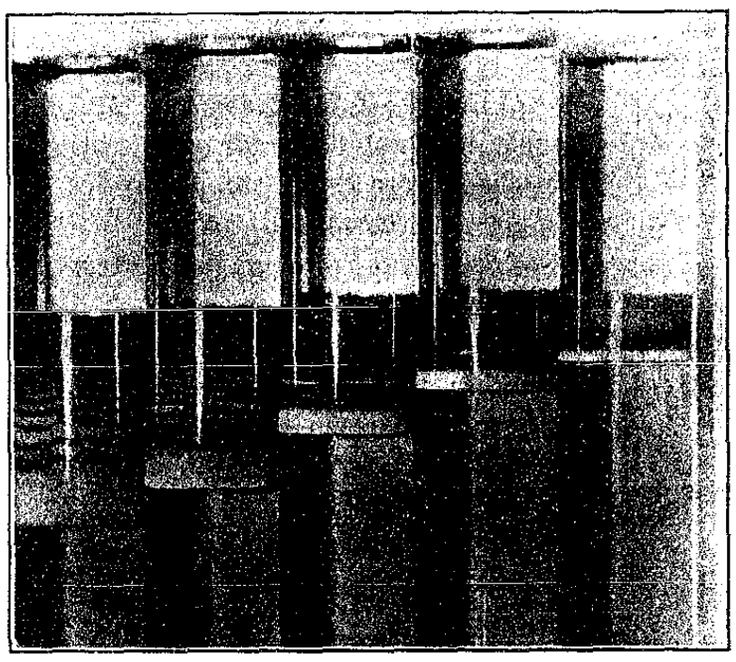


FIG. 2

Silver dichromate deposited in washed gelatine gel to which varying amounts of sodium chloride have been added; the amounts increase from left to right. The penetration decreases with increase in the amount of salt added.

The faded portion of the gel just under the deposit, is not so easily detected in *a*, *b*, and *c*, because the white haze interferes; viewing the tubes with blue light, the middle part of the haze is able to take on the blue tinge, hence it is white and the gel in which it lies is faded; the lower part of the gel has not faded. In the absence of other facts this would be evidence that the white haze formation is independent of the potassium dichromate.

The Zone Pattern formed by the Impurity in Gelatine: If a 4% commercial gelatine gel, without the dichromate addition, is made into cubes and these submerged in 1% silver nitrate, the center of the gel is cleared and the cleared zone extends to the corners; a white deposit, rather weak, is formed, as shown in Fig. 3 (taken against black paper). The zone pattern is well developed. Examination with a hand lens reveals fine lines in the deposit.

Dependence of the Red Silver Dichromate Bands on the Fine Lines of the Substructure: The non-formation of bands in the washed gelatine, and the reappearance of the bands on adding NaCl, prove conclusively that the red bands are dependent upon the fine lines of silver chloride. In the adjoined micro-photographs, Fig. 4, the two structures are shown; the camera was

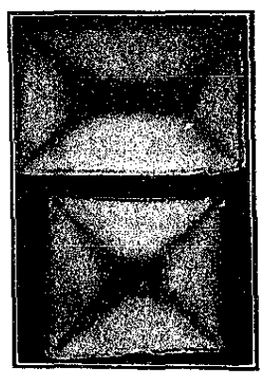


FIG. 3
The zone pattern formed by the chloride impurity in commercial gelatine with silver nitrate.



FIG. 4
Photomicrographs of the substructure of white lines and of the red bands of silver dichromate in gelatine. Magnification ×40.

moved from a point near the edge of a slice toward the center; the red bands become wider, are spaced wider, and become fainter as the center is approached. The fine hair lines similarly are wider, and becomes themselves wider and more diffuse, as the center is approached. The fine lines extend much further than the red bands, which is in keeping with the deeper penetration of the white haze in the test-tube experiments. The red bands are very evident, but the fine lines are easily missed, when sought visually, the camera exaggerates their effect, Fig. 4. In taking the micrographs, a wet slice of gelatine, freshly cut, was used; for all the other pictures, fresh wet slices were used; this procedure prevents mistaking a crystallised soluble salt, which might separate out on drying, for a structure which truly exists in the wet gel.

Liesegang[1] first noted the white, very fine lines formed in ordinary gelatine (on treatment with silver solution) and ascribed them to sodium chloride; but considered that the fine lines had no influence on the formation of the red bands.

Fritz Koehler[2] did extensive work in the study of the substructure, and decided that the fine lines were due to crystals of ammonium nitrate or potassium nitrate, the second product of the Liesegang reaction.

C. A. Schleussner[3] threw doubt on some of the evidence used by Koehler by indicating that the crystal shapes which play a part in Koehler's argument, were due to crystallisation on drying the gelatine, and did not exist in the wet gelatine. Schleussner found that adding citric acid increases the distance between the red bands, but had no influence on the white fine lines; additions of citric acid and sodium chloride, both together, and also separately, led him to the conclusion that the sodium chloride substructure was essential to ring formation. He used a washed gelatine, which however still contained halogens, "ausserst stark festgehalten". The method used in the present work, the removing all impurity, followed by the addition of known amounts, would seem to be simpler and more convincing.

[1] R. E. Liesegang, "Ueber die Schictungen bei Diffusionen" (1907); quoted from Koehler (see below); book not available.

[2] Fritz Koehler: Kolloid-Z., **19**, 65 (1916).

[3] C. A. Schleussner: Kolloid-Z., **31**, 347 (1922).

Miss Foster[1] investigated the effect of tap water and dilute bleaching powder solution on the Liesegang ring formation, more particularly on the substructure within the red rings. With pure water, the red rings showed no substructure, which may have been because the densest ones were studied (compare Fig. 4); several other observations are recorded which do not bear a clear relation to the present work.

Discussion: The formation of the zone pattern for the silver dichromate in washed gelatine, and for the chloride impurity in unwashed gelatine indicates that in both cases, the inner salt travels to the wall along straight lines; this was also the case with copper ferrocyanide.[2] To explain why the red bands must have the substructure of the fine lines due to silver chloride is not so easy. If the silver dichromate could be said to be a crystal, it would be easier, but although we have used the word deposit for silver dichromate, and although we feel certain that in some cases at least, a solid is formed, the terms "solid" and "dissolved" applied to gel structures are too loose to have scientific meaning. We intend to add to our information in this respect first, for only on a fullness of facts can a satisfactory theory be rested. It has been noted that the distance between the red rings is increased markedly when the tube is removed from the ice chest even for a short time; on the other hand, the net result for one cake kept at ice chest temperature is about the same as for another kept at room temperature, as Table I will indicate:

TABLE I

4% gelatine, with 0.1% $K_2Cr_2O_7$ inner salt, in cake form, submerged in 1% $AgNO_3$ outer salt

Different cakes, started at the same time.

	20°C		3.5°C	
In 15 min:	red bands, 6, ext. to	1.4 mm	4 bands, ext. to	1.3 mm
	ripples (fine lines)	.7 " further		.4
	haze with no structure	.45 " "		.4
		2.55		2.1
30 min:	red bands 8 more; ext. to	1.6 mm	7 bands, ext. to	1.85
	ripples	1.4 "		.6
	haze	.45		.55
		3.45		3.00
60 min:	red bands 8 more; ext. to	1.6 mm	10 bands, ext. to	2.65
	ripples	2.6 mm		1.05
	haze	indefinite		indefinite
		4.2		3.70
Total red bands		22		21
Total penetration		10.2 mm		8.71 mm

[1] Miss A. C. Foster: J. Phys. Chem., **23**, 645 (1920).
[2] Riegel and Widgoff: J. Phys. Chem., **29**, 872 (1925).

The age of the gelatine solution (up to 24 or 48 hours) has an effect on the gelatine in the experience of Schleussner[1], and in general our experience confirms this, but more exact information is needed.

Fine lines which, in a photograph at least, look just like the fine substructure due to the impurity, have been obtained by mere moistening followed by drying of a gelatine film.[2]

Summary: Silver dichromate in washed gelatine forms no line, but an unbroken deposit exhibiting the zone pattern similar to the one formed by copper ferrocyanide; the silver dichromate pattern is free from lines.

Addition of 0.1% NaCl (and smaller amounts) to the solution of washed gelatine causes a reappearance of the red bands; so that it may be said that the red bands do not form unless the substructure due to the chloride impurity is provided.

The chloride impurity itself forms a zone pattern with silver solution.

The penetration of the silver is less in a gelatine gel containing much NaCl, than in another containing only a trace.

Department of Chemistry
Foster Hall
University of Buffalo

[1] Kolloid-Z., **31**, 347 (1922).
[2] Schaum: Kolloid-Z., **36**, Zsigmondy Festschrift, 200 (1925).

THE FREE ENERGY CHANGE IN ADSORPTION AT A SOLID-VAPOUR INTERFACE

BY SAM LENHER AND IVAN ROY McHAFFIE

The change of free energy accompanying the adsorption of molecules of a vapour on a solid surface is an important thermodynamic function. The usefulness of this function would be greatly extended if some relation could be shown to exist between the free energy change and the number of molecules adsorbed per unit area of surface. What follows is an attempt to show this relationship in certain cases which have been recently studied by the authors.[1]

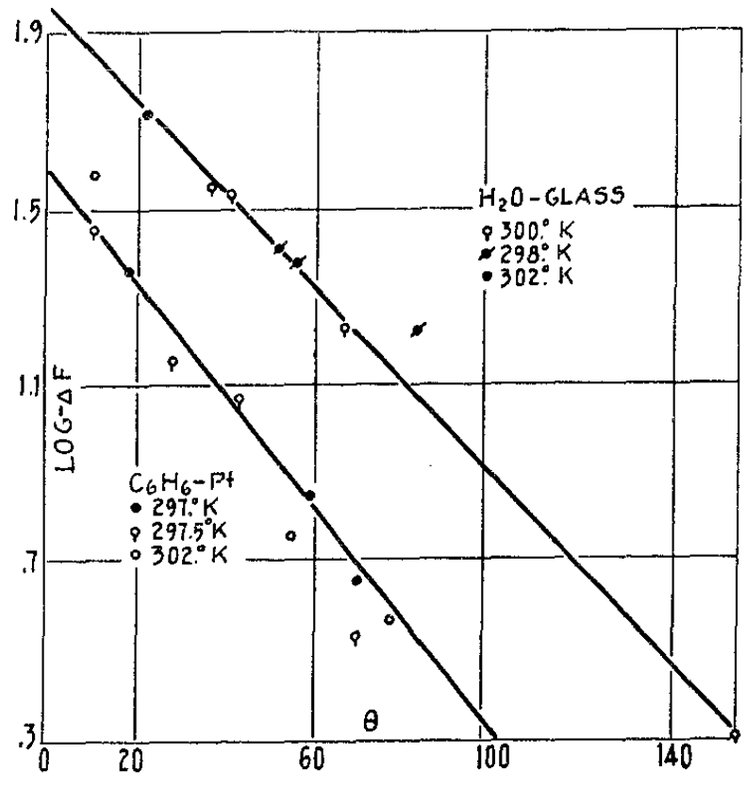


FIG. 1

The experimental method was such that the equilibrium vapour pressure of the adsorbed film at the temperature T was measured. Taking as a standard state that of pure vapour in equilibrium with liquid at the temperature T the change of free energy accompanying the adsorption of the vapour was calculated by means of the equation,

$$-\triangle\dot{F} = RT \log p/p_1 \qquad (1)$$

where p is the vapour pressure of the liquid at the standard state, and p_1 is the equilibrium pressure of the adsorbed film.

[1] McHaffie and Lenher: J. Chem. Soc., **127**, 1559 (1925); Lenher: **1926**, 1785; Lenher: Communication to the Chem. Soc., in press.

The amount of vapour adsorbed, expressed here in molecular layers θ, at the temperature T was calculated from the experimental data.

Using water and benzene numerous measurements of the adsorption of the vapours on solid surfaces of glass, silica, and platinum were carried out. Thus it was possible to determine at the temperature T the corresponding values of θ and $-\triangle F$. Since $-\triangle F$ refers to one gram molecule of the substance adsorbed at constant temperature, $-\triangle F$ must be a function of θ. An examination of the data showed that as θ increased $-\triangle F$ decreased and that the relationship was not a linear one. Two general expressions which might give this relation of θ and $-\triangle F$ are,

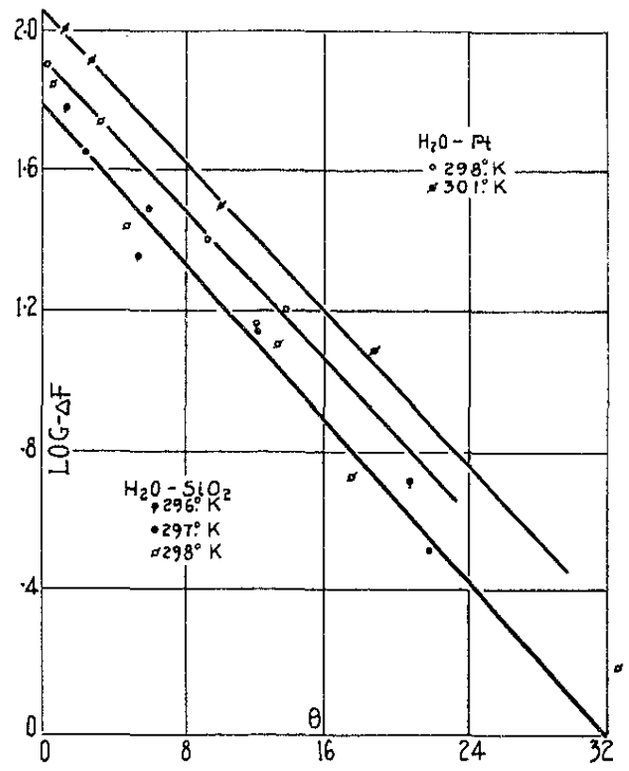


FIG. 2

$$-\triangle F = k_1 e^{-a\theta} \qquad (2)$$

$$-\triangle F = k_2/\theta^n \qquad (3)$$

It is evident that if equation (2) expresses this relationship the curve obtained by plotting log $(-\triangle F)$ against θ would be a straight line. In Fig. 1 log $(-\triangle F)$ and θ are plotted from the experimental data for water adsorbed on a glass surface and for benzene adsorbed on platinum at the temperatures indicated. Fig. 2 deals with similar data for water on silica and platinum.

The curves obtained for water on glass, benzene on platinum, water on silica, and water on platinum are straight lines. These curves represent the mean of the temperatures plotted, the variations of log $(-\triangle F)$ with temperature being very small over the range investigated. Only in the case of water on platinum were the isotherms at different temperatures clearly defined. The variation from the straight line is due, generally, to experimental error, but the range of validity of an equation of this type is limited. The lowest

values of θ for which such an equation appears to hold are from 2 to 5 molecular layers. At high values of θ, near saturation, where $-\triangle F$ approaches zero this equation does not hold. This follows since at a finite value of θ, $-\triangle F$ approaches zero and log $(-F\triangle)$ approaches negative infinity. For values of θ between these limits it has been found that $-\triangle F$ may be expressed as a function of θ by an equation of the form $-\triangle F = ke^{-a\theta}$.

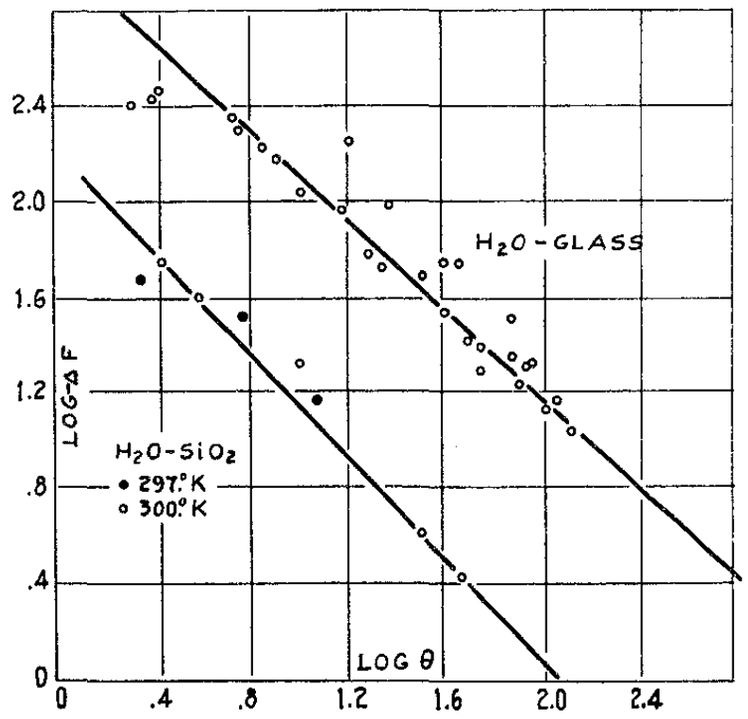


FIG. 3

The equations obtained from the curves of Figs. 1 and 2 are,

water on glass,	$-\triangle F_{300} = 93.4\ e^{-0.0249\theta}$
benzene on platinum	$-\triangle F_{298} = 40.7\ e^{-0.030\theta}$
water on silica,	$-\triangle F_{297} = 66.\ e^{-0.131\theta}$
water on platinum,	$-\triangle F_{298} = 87.\ e^{-0.123\theta}$
" "	$-\triangle F_{301} = 120.\ e^{-0.123\theta}$

To test the applicability of an equation of the type (3) log $(-\triangle F)$ was plotted against log θ, since if this equation expresses the relation existing between $-\triangle F$ and θ the curve obtained should be a straight line. These curves for water on glass and water on silica are shown in Fig. 3. The curve obtained for water on glass is a straight line. The relation existing is independent of the temperature at temperatures below 307°K; above this temperature the values of log $(-\triangle F)$ are all above the curve drawn.

The data for water on silica at 297°K and 300°K conform to the relation given by (3). The results for the adsorption of water on platinum and benzene on platinum were treated in a similar way but the deviation of the points plotted from the straight line function was much greater than that of the results shown in Fig. 3. The equations obtained for these curves are,

water on silica,	$-\triangle F = 162\theta^{-1.07}$
water on glass,	$-\triangle F = 1150\theta^{-0.943}$
water on platinum,	$-\triangle F = 275\theta^{-1.04}$
benzene on platinum	$-\triangle F = 214\theta^{-0.89}$

It is interesting to note that the exponent of θ in the four cases is nearly -1. The empirical equations presented express within stated limits the change of free energy with varying thickness of film adsorbed at a solid-vapour interface.

The authors wish to express to Professor F. G. Donnan, F. R. S. their appreciation of his advice and assistance.

Summary

A relation has been observed between the change of free energy and the amount of a vapour adsorbed per unit area of solid-vapour interface.

Two equations have been tested which give this relationship in certain cases.

Equations expressing $-\triangle F$ as a function of the number of molecular layers adsorbed are given for water on glass, silica, and platinum and for benzene on platinum.

The Sir William Ramsay Laboratories
of Physical and Inorganic Chemistry,
University College, London.
December 16, 1926.

THE REFRACTIVITY OF CARBON MONOXIDE

BY R. A. MORTON AND R. W. RIDING

It has long been known that the interaction between carbon monoxide and oxygen is greatly influenced by the presence or absence of water vapour. Reaction may occur photochemically or it may occur thermally by combustion or explosion.

Dixon[1] investigated the influence of water vapour when combination was effected by sparking between short platinum wires. He found that moist carbon monoxide-oxygen mixtures could be ignited over a very wide range of pressures. Elimination of water vapour brought about a progressive rise in ignition pressure indicating that, in the complete absence of moisture, ignition should not occur even under a continuous rain of sparks. Minute quantities of substances which yield water when sparked with oxygen (hydrogen sulphide, hydrogen chloride, ether, or hexane) acted in exactly the same manner as water in rendering the gaseous mixtures explosive. Compounds not containing hydrogen (including sulphur dioxide) appeared to have no influence on the reaction. The velocity of propagation of the explosion wave was observed to decrease with decreasing moisture content. Dixon regarded the water as a definitely chemical catalyst and suggested formic acid as the intermediate compound, since by passing sparks through moist carbon monoxide the acid is synthesised. Traube, however, draws attention to the formation of hydrogen peroxide.

The combustion of moist carbon monoxide and that of hydrogen have been studied by von Wartenberg and Sieg[2]. These authors established the occurrence of free hydrogen in the former reaction by its diffusion through platinum and they confirmed the presence of hydrogen peroxide in the latter reaction. Accordingly they advanced a step mechanism for the interaction between moist carbon monoxide and oxygen.

$$CO + H_2O \longrightarrow H.COOH$$
$$HCOOH \longrightarrow CO_2 + H_2$$
$$H_2 + O_2 \longrightarrow H_2O_2$$
$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Wieland has confirmed Dixon's recognition of the occurrence of formic acid, a result which gains further support from the work of Armstrong and Hilditch,[3] in which traces of the acid were obtained by the interaction of carbon monoxide and water at 350° in the presence of lime or ammonia. The equilibrium

$$H.COOH \rightleftharpoons CO + H_2O$$

has been studied at 156.1° and 217.9° by Branch,[4] using hydrogen chloride as a catalyst.

[1] Phil. Trans., **175**, 617 (1884); J. Chem. Soc., **49**, 94, 384 (1886).
[2] Ber., **53B**, *2192 (1920)*.
[3] Proc. Roy. Soc., **97A**, 267 (1920).
[4] J. Am. Chem. Soc., **37**, 2316 (1915).

Photochemical Reaction

Thiele[1] showed that carbon dioxide is decomposed by light into carbon monoxide and oxygen, a result confirmed by Berthelot and Gaudechon[2] and by Chadwick, Chapman and Ramsbottom.[3]

Coehn and Sieper[4] found that ultra-violet light of wave-length less than 254 μ brought about the reverse reaction. The degree of dissociation of carbon dioxide varied with the moisture content, the decomposition occurring only to 0.2% when the system was saturated with respect to water vapour at ordinary temperatures, and to about 18% when the gas was dried by means of phosphorus pentoxide. The rate of combination of carbon monoxide and oxygen was uninfluenced by the moisture content. Sulphur dioxide inhibited the decomposition of carbon dioxide by the agency of light. Coehn and Tramm[5] continued the work and found that moist carbon monoxide-oxygen mixtures could be ignited at almost any pressure by sparking. (Wartenberg and Sieg recorded a critical vapour pressure of 5 mm for water). Gaseous mixtures deprived of moisture by cooling with solid carbon dioxide and ether failed to explode but burned quietly if the cooling had not been prolonged. More thorough drying by the same means reduced the indications of combination to a faint bluish glow round the electrodes. A minute pressure change also occurred. Similar effects occurred in the photochemical reaction. Tramm[6] considers that the results point rather to a physical, than a purely chemical, role for the water vapour. He points out that on the basis of the Nernst Heat Theorem the concentration of formic acid in the moist carbon monoxide burning at 1000° C should not exceed 1 part in 20,000,000. The mechanism by which water catalyses the photochemical reaction may be concerned with its dipolar electrical nature—an opening of molecular fields of force on the lines of a Stark effect.

The reactivity of moist carbon monoxide must *either* receive an explanation of a special kind, peculiar to the substances reacting (i. e. the step mechanism) *or* it falls into line with the already long list of reactions profoundly affected by moisture.

There is no need to stress the fact that water occupies a unique position as an agency for chemical activation. It matters little whether the energy be supplied by thermal radiation or visible and ultra-violet radiation, the water acts in some way as the acceptor and distributor of energy which would in its absence be ineffective.

It therefore seems pertinent to enquire whether concomitant with the change in chemical reactivity a change in physical properties occurs. The observation of definite change in a property capable of accurate measurement might be expected to throw light on the mechanism of activation.

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[1] Ber., **40**, 4914 (1907).
[2] Compt. rend, **150**, 1690 (1910).
[3] J. Chem. Soc., **91**, 942 (1907).
[4] Z. physik. Chem., **41**, 356 (1916).
[5] Ber., **54B**, 1148 (1921).
[6] Z. physik. Chem., **105**, 356 (1923).

Such a property exists in the refractivity. Taylor[1] investigated the influence of side illumination on the refractivity of chlorine. In spite of special precautions to ensure the detection of very small effects the refractivity of illuminated chlorine appeared to be identical with that characterising the gas in its normal state.

In the present investigation on the influence of drying on the refractivity of carbon monoxide a Jamin refractometer made by Hilger was used in conjunction with a monochromator and a cadmium spark. An auxiliary source of white light was used so that the fringes due to the monochromatic light could be seen side by side with those due to the white light. The tube length was determined experimentally by counting the fringes passing across the field of view as dry air slowly entered the evacuated tube. If the refractive index for dry air at a wave-length λ is known the tube length is given by

$$P = N_{N.T.P.}\,\lambda/(\mu - 1)$$

μ = refractive index. P = length. $N_{N.T.P.}$ = number of fringes. The standard data of Meggers and Peters[2] were used. These authors showed that variations in the carbon dioxide content of the air were negligible. In our experiments the line 5085.83 Å was used throughout. At 760 mm, 15°C, the refractivity for this line, 2779.256×10^7, permits the length of our tube to be determined as 49.997 cms. Before proceeding to work on carbon monoxide the refractivity of oxygen was measured. Our value of 2717.28×10^7 differs from that calculated from Cuthbertson's data:[3]—2727.19×10^7. An explanation of the discrepancy was found in the different values for air.

Meggers and Peters $(\mu - 1) \times 10^7$	2931.96 at N.T.P.
Cuthbertson	2944.95.

Reducing Cuthbertson's value for oxygen we obtain $2715.9.10^7$ as against our result of $2717.28.10^7$, a difference of 5 in 10,000. In our determinations the maximum variation from the mean is 4 in 10,000. Carbon monoxide was now prepared by the interaction of formic and sulphuric acids, it was then passed over soda lime and through concentrated sulphuric acid. The entire apparatus was of glass, no rubber connections being used. The gas was passed through phosphorus pentoxide before use.

The mean of eight determinations of refractivity on the gas dried in this fashion was

$$(\mu - 1) \times 10^7 = 3366.60,$$

whilst the mean of two determinations on the gas further purified by liquefaction (fresh boiling liquid air) was

$$3366.35.$$

The refractivity of carbon monoxide containing 1 mm pressure of water vapour was next determined. The gas was passed through a special saturator

[1] Trans. Faraday Soc., **21**, 614 (1926).
[2] Bull. Bur. Standards (1918).
[3] Proc. Roy. Soc., **83A**, 160 (1910).

containing a sulphuric acid-water mixture.[1] Using the data of Cuthbertson for the refractive index of water vapour ($\mu - 1. 10^7 = 2538.0$ at 5085 Å) and assuming the simple mixture law, the refractivity of carbon monoxide at N. T. P. was obtained. Similar data were obtained when the carbon monoxide was saturated with water at room temperatures (16°-18°).

The results were as follows:—

No. of determinations		$(\mu-1) \times 10^7$ for 5085.83 Å	
a		3373.2	Cuthbertson
b		3363.33	Cuthbertson reduced to Meggers and Peters air value.
c	8	3366.60	Gas without liquefaction.
d	2	3366.35	After liquefaction.
e	1	3367.25	1 mm of water vapour
f		3366.24	with 14 mm "

The difference between *a* and *b* is due to the different value for air used in determining tube length.

The following values for the refractivity of carbon monoxide have also been obtained.

Observer	$(\mu-1) \times 10^7$ at 5461 Å
Mascart (1874)	3356
Perreau (1896)	3365
Koch (1909)	3361
Gruschcke (1910)	3361
Cuthbertson (1920)	3364

Our results are in accord with those of Cuthbertson if the tube length is determined from his data. The values of Meggers and Peters are preferred because of their agreement with the data of Howell[2] and Dickey.[3]

Since the refractivity is connected on the classical theory with a dispersional band in the Lyman region which has been identified with valency electrons (Drude) and ionisation potentials[4] it would seem as if the present results afford a basis for tentative conclusions on the mechanism of chemical activation.

Taylor's failure to observe any change in the refractivity of chlorine activated by illumination coupled with our failure to observe any change with carbon monoxide activated by water vapour point to the absence of any connexion between activation and valency electrons. It seems inevitable that we should regard activation as a process preceding ionisation or dissociation. Evidence for the real existence of such a predissociational state has been obtained by Henri and Teves[5] in an investigation of the absorption spectrum of sulphur vapour.

[1] Sorel: Z. angew. Chem., **1889**, 272.
[2] Phys. Rev., (2) **6**, 81 (1915).
[3] Astrophys. J., **45**, 188 (1917).
[4] Morton and Riding: Phil. Mag., (7) **1**, 726 (1926).
[5] Nature, **114**, 894 (1924).

It may be added that it was hoped to investigate the influence of even more intensive drying on the refractivity. As is well known the end plates used in interference work must be optically true and free from distortion. For intensive drying the end plates must be fused on to the tube and not maintained in position by sealing wax. It has so far proved impossible to obtain tubes free from distortional effects.

Summary

The effect of drying on the reactivity of carbon monoxide has been reviewed. The refractivity of oxygen for 5085.83 Å has been found to be 2717.28 $\times 10^7$ by means of a Jamin refractometer. This value is lower than that of Cuthbertson, but the discrepancy has been traced to a difference in the refractivity of air as determined by this author and Meggers and Peters, whose value we employed as the standard for fixing the length of tube.

The refractivity of carbon monoxide for 5085.83 Å was found to be 3366.6 $\times 10^7$. Mixtures of carbon monoxide and water vapour obey the simple mixture law, indicating that there is no change in the refractivity concomitant with the change in reactivity which is known to occur in the range of concentrations employed. It is suggested that activation is not concerned with valency electrons.

We express our thanks to Professor E. C. C. Baly, F. R. S. for much interest and advice and to the United Alkali Company for the generous terms of appointment which enabled one of us (R. W. R.) to participate in the work.

The University of Liverpool.
December 16, 1926.

SOLUBILITY OF COPPER SULPHATE, MALACHITE AND BURGUNDY PRECIPITATE IN AMMONIUM HYDROXIDE, CARBONATE AND BICARBONATE

BY E. B. HOLLAND AND G. M. GILLIGAN

Introduction

In connection with a rather extended investigation of copper fungicides it was found necessary to determine the solubility of various copper compounds in ammonium hydroxide, carbonate and bicarbonate, and the results so obtained are offered as a contribution to the literature on cuprammoniums.

As Penny (*17*, p. 5)[1] had shown 3.20 per cent ammonia (NH_3) the most efficient for malachite, approximately that concentration of ammonia was employed in all three solvents. The strength of the solvents was determined by adding a given quantity to an excess of normal acid, and titrating back with normal alkali, using methyl orange as indicator. Precautions were taken to prevent loss of ammonia from the standardized solutions, but occasional fortifying was found necessary. A temperature of 25°C. was adopted, but could not be maintained consistently in the laboratory. In all cases the copper salt was added to a measured quantity of approximately a 3.25 percent ammonia solvent in a 150 c.c. Erlenmeyer flask, stoppered, allowed to stand with occasional shaking to facilitate solution, diluted with water to 100 c.c., and final readings taken after several hours.

Solutions near saturation will often reprecipitate on standing, due to loss of ammonia from the liquid phase to the gaseous, therefore, the amount of solvent reported should exceed *slightly* that actually required for solution.

For convenience the various determinations will be classified, first, according to the solvent, into (1) ammonium hydroxide, (2) ammonium carbonate, (3) ammonium bicarbonate, and secondly, according to the source of copper into, (a) copper sulphate, (b) malachite, (c) Burgundy precipitate.

1. Ammonium Hydroxide

(*a*) *Copper Sulphate*

The amount of ammonium hydroxide (NH_4OH) and of ammonia (NH_3) required to give clear solutions with 1.0 gram and 0.1 gram of powdered, selected crystals of C. P. copper sulphate (Cu 25.37 per cent, equivalent to 99.66 per cent theoretical) dissolved in approximately 3.25 per cent solution of NH_3, and subsequently diluted to 100 c.c. and the calculated amount for each 100 c.c. of added water between these limits are reported in Table I.

[1] Reference is made by number (italic) to "Literature cited".

TABLE I

Ammonium hydroxide and ammonia required to give a clear solution with copper sulphate

Theoretical ratio		
Gram mols of ammonium hydroxide per mol of copper sulphate		0.14035
Gram mols of ammonia per mol of copper sulphate		0.06821
Gram mols of ammonium hydroxide per (n)[1] mols copper		0.55133
Gram mols of ammonia per (n)[1] mols copper		0.26793
Experimental data		
Copper sulphate to a clear solution in 100 c.c.	1.0 Gms.	0.1 Gms.
Mols of ammonium hydroxide	4.5	23.0
Mols of ammonia	4.5	23.0
Grams of ammonium hydroxide	0.63158	0.32281
Grams of ammonia	0.30695	0.15688
C.c. of commercial ammonia water (Sp. gr. 0.90)	1.26	0.65
Calculated		
Grams of ammonium hydroxide per 100 c.c. of water		0.28850
Grams of ammonia per 100 c.c. of water		0.14021
C.c. commercial ammonia water (Sp. gr. 0.90)		0.58

The amount of commercial ammonia water (Aqua Ammoniae Fortior) specific gravity 0.90, is calculated on the minimum requirement of the U. S. P. (*23*, pp. 56, 544) or 27 per cent ammonia (NH_3) by weight, equivalent to 0.2429 grams in 1 c.c. at 25°/25°C.

Millardet and David (*16*), Lasserre (*13*) and Butler (*2*, p. 238) obtained for 1 per cent solution of copper sulphate 1.53, 1.50 and 1.50 c.c. of ammonia water respectively, a quantity larger than was required in this laboratory. Horn (*12*, p. 476) cites 5.48 mols of ammonia for a 1.25 per cent solution. That a greater proportion of ammonia is required to maintain equilibrium on dilution is generally recognized, Pickering (*7*, p. 18) obtained 1.6 c.c. and Butler (*2*, p. 238) 0.7 c.c. of ammonia water for a 0.1 per cent solution of copper sulphate, results appreciably higher than that reported.

There is naturally a difference of opinion as to the reactions involved in the production of cuprammonium sulphate, but the following are intended to embrace substantially the views of Chester (*4*, p. 68), Dawson and McCrae (*5*, p. 1258; *6*, p. 1666), Horn (*12*, p. 475) and Prescott and Johnson (*22*, p. 106).

(1) $4CuSO_45H_2O + 6NH_4OH = CuSO_4.3Cu(OH)_2.H_2O + 3(NH_4)_2SO_4 + 19H_2O$

(2) $CuSO_4.3Cu(OH)_2.H_2O + 3(NH_4)_2SO_4 + 2NH_4OH = 4Cu(OH)_2 + 4(NH_4)_2SO_4 + H_2O$

(3) $4Cu(OH)_2 + 4(NH_4)_2SO_4 + (8+n)NH_4OH = 4Cu(NH_3)_2(OH)_2 + 4(NH_4)_2SO_4 + n(NH_4OH) + 8H_2O$

[1] The number of mols of copper in the compound.

(4) $4Cu(NH_3)_2(OH)_2 + 4(NH_4)_2SO_4 + n(NH_4OH) = 4Cu(NH_3)_4SO_4 H_2O + n(NH_4OH) + 4H_2O$

(5) $4Cu(NH_3)_4SO_4H_2O + 5H_2O = CuSO_4.3Cu(OH)_2.H_2O + 3(NH_4)_2 SO_4 + 10NH_4OH$

By analogy one may presuppose in reaction (1) $5CuO \cdot SO_3$ and $10CuO$ SO_3 from 6.4 mols and 7.2 mols of ammonia as in the case of fixed alkalies, shown by Pickering (*18*, p. 1983; *19*, pp. 1991, 1997, 2000; *21*, pp. 1852, 1855; *9*, pp. 26, 27), but there is no evidence to that effect. In reaction (3) (n) must be 0.5 mols per mol of copper sulphate for a 1 per cent solution, as shown in Table I, but as (n) increases rapidly on dilution, dissociation phenomena must be involved. Furthermore dry commercial cuprammonium sulphate, $Cu(NH_3)_4SO_4.H_2O$, although an unstable product, required only a small amount of additional ammonia to clear a 1 per cent solution which would tend to confirm the value of (n).

Theoretically the precipitate obtained on dilution, reaction (5), should be largely basic sulphate, but in some instances at least considerable hydroxide results which on filtering and drying is readily converted into basic carbonate, as shown by the analysis of the following sample prepared in the laboratory.

	Per cent
Cupric oxide, CuO	69.47
Sulphuric trioxide, SO_3	6.72
Carbon dioxide, CO_2	9.27
Water by difference, H_2O	14.54
	100.00

Hypothetical combinations

Water, H_2O	2.606
Tribasic copper sulphate, $4CuO.SO_3.4H_2O$	39.483
Basic copper carbonate, $CuCO_3.Cu(OH)_2$	46.594
Copper hydroxide, $Cu(OH)_2$	11.317
	100.000

With proper control, however, and less attention to yield a higher proportion of basic sulphate should be recovered.

The solubility of tribasic copper sulphate ($4CuO.SO_3.4H_2O$) in ammonia could not be determined as a sample of satisfactory quality was not obtainable at the time.

(*b*) *Malachite*

The amount of ammonium hydroxide and of ammonia required to give clear solutions with 0.5 gram and 0.1 gram of Merck's, C. P., green copper carbonate (moisture 1.58 per cent, Cu 54.30 per cent, equivalent to 94.45 per cent pure) dissolved in approximately 3.25 per cent solution of ammonia,

and subsequently diluted to 100 c.c., and the calculated amount for each 100 c.c. of added water between these limits are reported in Table II. As the quantity of 3.25 per cent ammonia necessary for 1 gram of malachite would exceed 100 c.c., 0.5 gram was the maximum amount employed. Technical or commercial malachite is said to contain only 50 to 52 per cent of copper.

TABLE II

Ammonium hydroxide and ammonia required to give a clear solution with malachite

Theoretical ratio	
Gram mols of ammonium hydroxide per mol of malachite	0.15848
Gram mols of ammonia per mol of malachite	0.07701
Gram mols of ammonium hydroxide per (n)[1] mols of copper	0.27566
Gram mols of ammonia per (n)[1] mols of copper	0.13396

Experimental data		
Malachite to a clear solution in 100 c.c.	0.5 Gms.	0.1 Gms.
Mols of ammonium hydroxide	60.0	65.0
Mols of ammonia	60.0	65.0
Grams of ammonium hydroxide	4.75440	1.03012
Grams of ammonia	2.31030	0.50057
C.c. of commercial ammonia water (Sp. gr. 0.90)	9.51	2.06

Calculated	
Grams of ammonium hydroxide per 100 c.c. of water	0.09905
Grams of ammonia per 100 c.c. of water	0.04814
C.c. of commercial ammonia water (Sp. gr. 0.90)	0.20

Investigators do not agree as to the reaction involved in the solution of malachite in ammonia. Gastine (*11*, p. 115) claims the resultant is cuprammonium carbonate; Pickering (*8*, p. 20) mainly cuprammonium carbonate; Chester (*4*, p. 68) cuprammonium carbonate and cuprammonium hydroxide, and Butler (*2*, p. 242) cuprammonium hydroxide. Mellor (*15*, pp. 151, 152, 275) cites considerable data, but to what extent applicable is uncertain. Evidently cuprammonium carbonate could not be formed in entirety unless sufficient carbon dioxide was absorbed to satisfy the reaction (1), but a mixture of cuprammonium carbonate and of cuprammonium hydroxide (2), or cuprammonium hydroxide alone, (3) offers a more feasible hypothesis.

(1) $CuCO_3.Cu(OH)_2 + CO_2 + 4NH_4OH = 2Cu(NH_3)_2CO_3 + 5H_2O$

(2) $CuCO_3.Cu(OH)_2 + 6NH_4OH = Cu(NH_3)_2CO_3 + Cu(NH_3)_4(OH)_2 + 6H_2O$

(3) $CuCO_3.Cu(OH)_2 + 9NH_4OH = 2Cu(NH_3)_4(OH)_2 + NH_4HCO_3 + 7H_2O$

[1] The number of mols of copper in the compound.

As the amount of ammonia entering combination constitutes but a small proportion of that required for solution, due probably to limited surface area, and the resistance of malachite to dissociation, the mols reported, Table II, are of little significance in designating the reaction. Reaction (3) seems the most probable, however, as the solution dissolves cellulose, does not deposit malachite on standing, according to Butler (*2*, p. 242), and yields the hydroxide on dilution. A precipitate prepared in the laboratory by dilution, filtration, and drying in vacuo at room temperature, gave a blue resultant which contained 61.98 per cent of copper, and a trace of carbon dioxide equivalent to about 95 per cent cupric hydroxide. The carbon dioxide content must vary with the conditions of precipitation and exposure. The cuprammonium hydroxide formed with a small excess of ammonia is presumably the diammino obtained by Dawson and McCrae (*5*, p. 1257), and by Bonsdorff (*1*), but with a large excess of ammonia the tetrammino is more probable as shown by Bonsdorff.

The solubility of azurite ($2CuCO_3.Cu(OH)_2$) in ammonia could not be determined as the only sample available contained 12.12 per cent of ammonia insoluble matter which masked the end point.

(c) *Burgundy Precipitate*

The amount of ammonium hydroxide and of ammonia required to give clear solutions with aliquots of washed Burgundy precipitate, equivalent to 1.0 gram and 0.1 gram of copper sulphate, dissolved in approximately 3.25 per cent solution of ammonia, NH_3, and subsequently diluted to 100 c.c. and the calculated amount for each 100 c.c. of added water between these limits, are reported in Table III.

The Burgundy mixture (soda Bordeaux, bouillie Bourguignonne) was prepared according to Masson (*14*, p. 816) as modified by Pickering (*10*, p. 86; *20*, pp. 1412, 1414, 1428).

$$5CuSO_45H_2O + 8Na_2CO_310H_2O = 5CuO.2CO_2.6H_2O + 5Na_2SO_410H_2O + 6NaHCO_3 + 46H_2O$$

Particular care was observed in gradually adding a *cool*, dilute solution of copper sulphate to a similar solution of sodium carbonate in order to reduce the loss of carbon dioxide to a minimum, and to favor the formation of a basic carbonate. The reverse procedure is likely to yield more or less basic sulphate. The precipitate was allowed to coalesce, filtered, washed substantially free from sodium sulphate and sodium bicarbonate, transferred to a graduated flask, and made to volume. Upon standing the washed precipitate is gradually converted into malachite. The results are reported in terms of copper sulphate, less small unavoidable errors due to incomplete precipitation of the copper and mechanical losses, but assuming that one gram of copper sulphate yields approximately 0.47570 grams of basic carbonate ($5CuO.2CO_2.6H_2O$) the results could be readily recalculated to the latter basis.

TABLE III

Ammonium hydroxide and ammonia required to give a clear solution with washed Burgundy precipitate, in terms of copper sulphate

Theoretical ratio		
Gram mols of ammonium hydroxide per mol of copper sulphate		0.14035
Gram mols of ammonia per mol of copper sulphate		0.06821
Gram mols of ammonium hydroxide per (n) mols of copper		0.55133
Gram mols of ammonia per (n) mols of copper		0.26793
Experimental data		
Copper sulphate to a clear solution in 100 c.c.	1.0 Gms.	0.1 Gms.
Mols of ammonium hydroxide	18.5	34.0
Mols of ammonia	18.5	34.0
Grams of ammonium hydroxide	2.59648	0.47719
Grams of ammonia	1.26189	0.23191
C.c. of commercial ammonia water (Sp. gr. 0.90)	5.20	0.95
Calculated		
Grams of ammonium hydroxide per 100 c.c. of water		0.24171
Grams of ammonia per 100 c.c. of water		0.11747
C.c. of commercial ammonia water (Sp. gr. 0.90)		0.48

The reaction for solution is presumably similar to that of malachite.

The solubility of sodium bicarbonate Bordeaux (Bordeaux bouillie celeste), (*3*, p. 291; *20*, p. 1414) precipitate in ammonia was not determined as the precipitation was considered too variable and incomplete to warrant the examination.

The solubility on a one per cent basis of copper sulphate, malachite and washed Burgundy precipitate, and of the copper present, in ammonium hydroxide and its ammonia content, is summarized in Table IV, together with the dilution or hydrolytic equivalent.

TABLE IV

Solubility and hydrolytic equivalent of the copper compounds in ammonium hydroxide

On a one per cent basis	Ammonium hydroxide Grams	Ammonia Grams
Copper sulphate	0.63158	0.30695
Hydrolytic equivalent per 100 c.c., 1.0 to 0.1 gram	0.28850	0.14021
Copper in copper sulphate[1]	2.48948	1.20989
Hydrolytic equivalent	1.13717	0.55266
Malachite	9.50880	4.62060
Hydrolytic equivalent per 100 c.c., 0.5 to 0.1 gram	0.09905	0.04814
Copper in malachite[1]	17.51160	8.50939
Hydrolytic equivalent	0.18241	0.08866
Washed Burgundy precipitate	5.45823	2.65270
Hydrolytic equivalent per 100 c.c., 0.48 to 0.048 gram	0.24171	0.11747
Copper in washed Burgundy precipitate	10.23482	4.97412
Hydrolytic equivalent	0.45323	0.22027

[1] Calculated on a theoretical basis from the copper in the product tested.

Summary of Results with Ammonium Hydroxide

1. The solubility of malachite, washed Burgundy precipitate, and copper sulphate in ammonium hydroxide, increases in the order named or directly with their dispersion. Conversely the amount of ammonium hydroxide required to form soluble cuprammonium decreases in the same order.

2. The solubility of the copper in ammonia is in the same order but more uniform.

3. Ammonium hydroxide soluble cuprammoniums are unstable on dilution. The "hydrolytic equivalent" or the amount of solvent required to counteract dilution, is in the reverse order of the solubilities and, in terms of copper and of ammonia, fairly proportional.

4. Ammonium hydroxide soluble cuprammoniums are unstable in relatively high concentrations of ammonia, and under the influence of heat, decomposing with the formation of dicupric hydroxide or oxide.

2. Ammonium Carbonate

The solubility of the several copper compounds in ammonium carbonate was determined in the same manner as in ammonium hydroxide. Ammonium carbonate (Ammonii Carbonas) consists of varying proportions of ammonium bicarbonate (NH_4HCO_3) and ammonium carbamate ($NH_4.NH_2CO_2$), but is generally considered as of equal mols and substantially of equal parts by weight 79.048: 78.064. The amount of commercial ammonium carbonate is calculated on the minimum requirement of the U. S. P. (*23*, pp. 47, 48)—"to yield 30 per cent of ammonia (NH_3)" by weight, equivalent to 92.245 per cent theoretical. A solution of approximately 3.25 per cent ammonia (NH_3) content was employed and the copper salt added to the solvent, aiming to produce cuprammonium carbonate. Loss of carbon dioxide could not be entirely prevented however.

(*a*) *Copper Sulphate*

TABLE V

Ammonium carbonate required to give a clear solution with copper sulphate

	Theoretical ratio	
Gram mols of ammonium carbonate per mol of copper sulphate		0.62917
Gram mols of ammonia per mol of copper sulphate		0.06821
Gram mols of ammonium carbonate per (n) mols of copper		2.47148
Gram mols of ammonia per (n) mols of copper		0.26793
	Experimental data	
Copper sulphate to a clear solution in 100 c.c.	1.0 Gms.	0.1 Gms.
Mols of ammonium carbonate	2.5	3.0
Mols of ammonia	7.5	9.0
Grams of ammonium carbonate	1.57293	0.18875
Grams of ammonia	0.51158	0.06139
Grams of commercial ammonium carbonate	1.71	0.20

TABLE V (continued)

Calculated	
Grams of ammonium carbonate per 100 c.c. of water	0.03495
Grams of ammonia per 100 c.c. of water	0.01137
Grams of commercial ammonium carbonate	0.04

Assuming that cuprammonium carbonate is formed in entirety, the following tentative reaction, complying with the results obtained with a one per cent solution of copper sulphate, Table V, is suggested:

$$_2CuSO_45H_2O + 5NH_4HCO_3NH_4NH_2CO_2 = 2Cu(NH_3)_2CO_3 + 2(NH_4)_2SO_4 + 7NH_4HCO_3 + CO_2 + 6H_2O$$

Four mols of ammonium carbonate to 3 of copper sulphate would satisfy the equation, but evidently greater excess is necessary for the reaction under the conditions employed. On evaporation the solution appears to yield malachite.

$$_2Cu(NH_3)_2CO_3 + 2(NH_4)_2SO_4 + H_2O = CuCO_3 . Cu(OH)_2 + 2(NH_4)_2SO_4 + 4NH_3 + CO_2$$

A one per cent solution of commercial cuprammonium sulphate required about 0.5 mols of ammonium carbonate per mol of sulphate to clear, in which case only a small proportion at best could have been converted into cuprammonium carbonate.

(*b*) *Malachite*

TABLE VI

Ammonium carbonate required to give a clear solution with malachite

Theoretical ratio	
Gram mols of ammonium carbonate per mol of malachite	0.71041
Gram mols of ammonia per mol of malachite	0.07701
Gram mols of ammonium carbonate per (n) mols of copper	1.23574
Gram mols of ammonia per (n) mols of copper	0.13396

Experimental data		
Malachite to a clear solution in 100 c.c.	1.0 Gms.	0.1 Gms.
Mols of ammonium carbonate	5.0	5.0
Mols of ammonia	15.0	15.0
Grams of ammonium carbonate	3.55205	0.35521
Grams of ammonia	1.15515	0.11552
Grams of commercial ammonium carbonate	3.85	0.39

Calculated	
Grams of ammonium carbonate per 100 c.c. of water	0.00000
Grams of ammonia per 100 c.c. of water	0.00000
Grams of commercial ammonium carbonate	0.00000

The following tentative reaction is suggested as complying with the results secured with a one per cent solution, Table VI.

$$CuCO_3.Cu(OH)_2 + 5NH_4HCO_3NH_4NH_2CO_2 + 5H_2O = 2Cu(NH_3)_2CO_3 + 9NH_4HCO_3 + 2NH_4OH$$

Four mols of ammonium carbonate to 3 mols of malachite would furnish sufficient ammonia to satisfy the equation but not for the reaction. On evaporation the solution apparently yields malachite or other basic carbonate.

(c) *Burgundy Precipitate*

The washed Burgundy precipitate was prepared as previously described, and the solubility determined on aliquots. The results are reported in terms of copper sulphate, but may be recalculated to basic carbonate ($5CuO.2CO_2.6H_2O$), assuming that 1 gram of copper sulphate yields approximately 0.47570 grams of basic carbonate.

TABLE VII

Ammonium carbonate required to give a clear solution with washed Burgundy precipitate, in terms of copper sulphate

Theoretical ratio		
Gram mols of ammonium carbonate per mol of copper sulphate		0.62917
Gram mols of ammonia per mol of copper sulphate		0.06821
Gram mols of ammonium carbonate per (n) mols of copper		2.47148
Gram mols of ammonia per (n) mols of copper		0.26793
Experimental data		
Copper sulphate to clear solution in 100 c.c.	1.0 Gms.	0.1 Gms.
Mols of ammonium carbonate	3.33	3.33
Mols of ammonia	10.0	10.0
Grams of ammonium carbonate	2.09723	0.20972
Grams of ammonia	0.68210	0.06821
Grams of commercial ammonium carbonate	2.27	0.23
Calculated		
Grams of ammonium carbonate per 100 c.c. of water		0.00000
Grams of ammonia per 100 c.c. of water		0.00000
Grams of commercial ammonium carbonate		0.00000

The solubility, on a one per cent basis, of copper sulphate, malachite and washed Burgundy precipitate and of the copper present, in ammonium carbonate and its ammonia content is summarized in Table VIII, together with the dilution or hydrolytic equivalent.

TABLE VIII

Solubility and hydrolytic equivalent of the copper compounds in ammonium carbonate

On a one per cent basis	Ammonium carbonate	Ammonia
	Grams	Grams
Copper sulphate	1.57293	0.51158
Hydrolytic equivalent per 100 c.c., 1.0 to 0.1 gram	0.03495	0.01137
Copper in copper sulphate[1]	6.19996	2.01648
Hydrolytic equivalent	0.13776	0.04482
Malachite	3.55205	1.15515
Hydrolytic equivalent per 100 c.c., 1.0 to 0.1 gram	0.00000	0.00000
Copper in malachite[1]	6.54144	2.12735
Hydrolytic equivalent	0.00000	0.00000
Washed Burgundy precipitate	4.40872	1.43389
Hydrolytic equivalent per 100 c.c., 0.48 to 0.048 gram	0.00000	0.00000
Copper in washed Burgundy precipitate	8.26687	2.68871
Hydrolytic equivalent	0.00000	0.00000

Summary of Results with Ammonium Carbonate

1. The solubility of washed Burgundy precipitate, malachite and copper sulphate in ammonium carbonate increased in the order named, but is more uniform than in the case of ammonium hydroxide. The lower solubility of Burgundy precipitate ($5CuO.2CO_2.6H_2O$) as compared with malachite ($CuCO_3.Cu(OH)_2$) may be due in part to the lower ratio of CO_2: Cu, as the physical character of the former is naturally more promising.

2. The solubility of the copper in terms of ammonia is fairly constant, and in marked contrast to ammonium hydroxide in this respect.

3. Ammonium carbonate soluble cuprammoniums are more stable on dilution than the ammonium hydroxide soluble. Copper sulphate required a small excess of solvent to prevent partial hydrolysis, but malachite and Burgundy precipitate did not require any between the limits tested.

4. Ammonium carbonate soluble cuprammoniums are less likely to decompose with the formation of cupric oxide than ammonium hydroxide soluble.

3. Ammonium Bicarbonate

Ammonium bicarbonate (NH_4HCO_3) was also employed as a solvent in the same way as ammonium carbonate. There is no prescribed standard, but as the compound is relatively more stable than the carbonate, 95 per cent of the theoretical ammonia content was adopted as a reasonable requirement for the commercial product, equivalent to 20.47 per cent of ammonia (NH_3) by weight.

[1] Calculated on a theoretical basis from the copper in the product tested.

(*a*) *Copper Sulphate*

TABLE IX

Ammonium bicarbonate required to give a clear solution with copper sulphate

Theoretical ratio		
Gram mols of ammonium bicarbonate per mol of copper sulphate	0.31655	
Gram mols of ammonia per mol of copper sulphate	0.06821	
Gram mols of ammonia bicarbonate per (n) mols of copper	1.24348	
Gram mols of ammonia per (n) mols of copper	0.26793	
Experimental data		
Copper sulphate to a clear solution in 100 c.c.	1.0 Gms.	0.1 Gms.
Mols of ammonium bicarbonate	8.5	12.0
Mols of ammonia	8.5	12.0
Grams of ammonium bicarbonate	2.69068	0.37986
Grams of ammonia	0.57979	0.08185
Grams of commercial ammonium bicarbonate	2.83	0.40
Calculated		
Grams of ammonium bicarbonate per 100 c.c. of water		0.11199
Grams of ammonia per 100 c.c. of water		0.02666
Grams of commercial ammonium bicarbonate		0.13

The following tentative reaction is suggested as complying with the results obtained with a one per cent solution, Table IX.

$2CuSO_45H_2O + 17NH_4HCO_3 = 2Cu(NH_3)_2CO_3 + 2(NH_4)_2SO_4 + 9NH_4HCO_3 + 6CO_2 + 16H_2O$

Four mols of ammonium bicarbonate to 1 mol of copper sulphate would furnish sufficient ammonia to satisfy the equation, but not for the reaction.

(*b*) *Malachite*

TABLE X

Ammonium bicarbonate required to give a clear solution with malachite

Theoretical ratio		
Gram mols of ammonium bicarbonate per mol of malachite	0.35743	
Gram mols of ammonia per mol of malachite	0.07701	
Gram mols of ammonium bicarbonate per (n) mols of copper	0.62174	
Gram mols of ammonia per (n) mols of copper	0.13396	
Experimental data		
Malachite to a clear solution in 100 c.c.	0.5 Gms.	0.1 Gms.
Mols of ammonium bicarbonate	15.0	15.0
Mols of ammonia	15.0	15.0
Grams of ammonium bicarbonate	2.68073	0.53615
Grams of ammonia	0.57758	0.11552
Grams of commercial ammonium bicarbonate	2.82	0.56

TABLE X (continued)

Calculated	
Grams of ammonium bicarbonate per 100 c.c. of water	0.00000
Grams of ammonia per 100 c.c. of water	0.00000
Grams of commercial ammonium bicarbonate	0.00000

As the quantity of solvent necessary for one gram of malachite would exceed 100 c.c., 0.5 gram was the maximum amount employed.

The following tentative reaction is suggested as complying with the results obtained with a 0.5 per cent solution, Table X.

$$CuCO_3.Cu(OH)_2 + 15NH_4HCO_3 = 2Cu(NH_3)_2CO_3 + 11NH_4HCO_3 + 3CO_2 + 5H_2O$$

Four mols of ammonium bicarbonate to 1 mol of malachite would furnish sufficient ammonia to satisfy the reaction.

(c) *Burgundy Precipitate*

TABLE XI

Ammonium bicarbonate required to give a clear solution with washed Burgundy precipitate, in terms of copper sulphate

Theoretical ratio	
Gram mols of ammonium bicarbonate per mol of copper sulphate	0.31655
Gram mols of ammonia per mol of copper sulphate	0.06821
Gram mols of ammonium bicarbonate per (n) mols of copper	1.24348
Gram mols of ammonia per (n) mols of copper	0.26793

Experimental data		
Copper sulphate to a clear solution in 100 c.c.	1.0 Gms.	0.1 Gms.
Mols of ammonium bicarbonate	10.0	10.0
Mols of ammonia	10.0	10.0
Grams of ammonium bicarbonate	3.16550	0.31655
Grams of ammonia	0.68210	0.06821
Grams of commercial ammonium bicarbonate	3.33	0.33

Calculated	
Grams of ammonium bicarbonate per 100 c.c. of water	0.00000
Grams of ammonia per 100 c.c. of water	0.00000
Grams of commercial ammonium bicarbonate	0.00000

The solubility, on a one per cent basis, of copper sulphate, malachite and washed Burgundy precipitate and of the copper present in ammonium bicarbonate and its ammonia content, is summarized in Table XII, together with the dilution or hydrolytic equivalent.

TABLE XII
Solubility and hydrolytic equivalent of the copper compounds in ammonium bicarbonate

On a one per cent basis	Ammonium bicarbonate	Ammonia
	Grams	Grams
Copper sulphate	2.69068	0.57979
Hydrolytic equivalent per 100 c.c., 1.0 to 0.1 gram	0.11199	0.02666
Copper in a copper sulphate[1]	10.60576	2.28534
Hydrolytic equivalent	0.44143	0.10508
Malachite	5.36146	1.15516
Hydrolytic equivalent per 100 c.c., 0.5 to 0.1 gram	0.00000	0.00000
Copper in malachite[1]	9.87378	2.12737
Hydrolytic equivalent	0.00000	0.00000
Washed Burgundy precipitate	6.65440	1.43389
Hydrolytic equivalent per 100 c.c., 0.48 to 0.048 gram	0.00000	0.00000
Copper in washed Burgundy precipitate	12.47778	2.68871
Hydrolytic equivalent	0.00000	0.00000

Summary of Results with Ammonium Bicarbonate

1. The solubility of washed Burgundy precipitate, malachite and copper sulphate in ammonium bicarbonate increased in the order named, and is even more uniform than with ammonium carbonate. The bicarbonate, however, proved less efficient than the carbonate.

2. The solubility of the copper in terms of ammonia is nearly constant, but in a new order malachite, copper sulphate and Burgundy precipitate.

The same amount of ammonia in bicarbonate and carbonate proved equally effective on the copper in malachite and on the copper in Burgundy precipitate, but the ammonia in the bicarbonate is less effective than in the carbonate, on the copper in copper sulphate.

3. In the case of copper sulphate more bicarbonate was required to prevent hydrolysis than of carbonate, but with malachite and Burgundy precipitate no additional solvent was required between the limits tested.

Summary of Results with the Different Solvents

1. The effectiveness of ammonium bicarbonate, ammonium carbonate and ammonium hydroxide on copper sulphate in producing soluble cuprammoniums increases in the order named, and hold equally true of the ammonia content, but not in the same magnitude.

2. The effectiveness of ammonium hydroxide, ammonium bicarbonate and ammonium carbonate on malachite increases in the order named, but the ammonia in carbonate and bicarbonate is equally effective.

3. The effectiveness of ammonium bicarbonate, ammonium hydroxide and ammonium carbonate on Burgundy precipitate increased in the order named, but the ammonia in carbonate and bicarbonate is equally effective.

[1] Calculated on a theoretical basis from the copper in the product tested.

4. The hydrolytic equivalent of the cuprammoniums decreases in the following order, copper sulphate-ammonium hydroxide, Burgundy precipitate-ammonium hydroxide, copper sulphate-ammonium bicarbonate, malachite-ammonium hydroxide, and copper sulphate-ammonium carbonate. Malachite and Burgundy precipitate with ammonium carbonate and ammonium bicarbonate required no additional solvent between the limits tested. In terms of ammonia malachite-ammonium hydroxide preceded copper sulphate-ammonia bicarbonate, otherwise in the same order as above. In general the hydrolytic equivalent was inversely proportional to the amount required for solution.

Mass. Agricultural Exp. Station,
Amherst, Mass.

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MUTAROTATION. I.

Velocity of Mutarotation of α Glucose in Methyl Alcohol and Water

BY FREDERICK PALLISER WORLEY AND JOHN CLARK ANDREWS

The mutarotation of sugars has received a great deal of attention during recent years, and various explanations of the mechanism of the action have been advanced, but none of these explanations has been found entirely satisfactory, nor have they received wide acceptance. Baker, Ingold and Thorpe[1] stimulated interest in the problem by an attempted critical investigation of the explanations of the mechanism of mutarotation advanced by E. F. Armstrong[2], Lowry[3] and Jacobsen and Stelzner[4]. The present investigation was undertaken with a view to criticising conclusions arrived at by Baker, Ingold and Thorpe. Lowry[5] in the meantime has adversely criticized their work and has pointed out that their mathematical investigation of the problem is unsound. He also advanced the subject by pointing out the similarity between mutarotation and the hydrolysis and saponification of esters.

In spite of the large amount of experimental work already carried out by numerous investigators it would appear that all the facts necessary for the solution of the problem have not been available, and a considerable amount of work has recently been carried out using various sugars and their methylated and other derivations in various solvents.[6]

The experimental basis of the work of Baker, Ingold and Thorpe was the effect of water on the velocity of mutarotation of α glucose in methyl alcohol. The proportion of water did not exceed 2% and no account was taken, as was pointed out by Lowry, of minute accounts of catalysts present. It appeared desirable to ascertain the velocity in mixtures of highly purified methyl alcohol and water in all proportions. This has been done in the present investigation but although special care was taken in the purification of materials used it is not likely that all traces of catalytic substances have been removed. Even were it possible to obtain the substances absolutely pure, unavoidable contact with the atmosphere introduces impurities likely to have some catalytic action.

Purification of Materials

α Glucose was three times recrystallised from specially purified ethyl alcohol, final traces of alcohol being removed by careful warming under reduced pressure. The product was stored in a flask connected to a second flask containing phosphorus pentoxide.

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[1] J. Chem. Soc., **125**, 268 (1924).
[2] J. Chem. Soc., **85**, 1567 (1904).
[3] J. Chem. Soc., **83**, 1316 (1903).
[4] "Organische Chemie", 2nd Ed., (1) **2**, 866, 910, 915, 927.
[5] J. Chem. Soc., **127**, 1371 (1925).
[6] Lowry and Richards: J. Chem. Soc., **127**, 1385; Lowry and Faulkner: 2883 (1925); Jones and Lowry: **128**, 720; Faulkner and Lowry: 1938 (1926).

Methyl alcohol A. R. obtained from British Drug Houses, was found to contain traces of acetone. The acetone was converted into iodoform by means of iodine and caustic potash. After filtering, the liquid was refluxed for eight hours over freshly burnt lime. It was then distilled through a Young's Evaporator column of eight sections and the middle portion collected in a waxed vessel after condensation in a condenser having an inner tube of silica. The boiling point was constant 64.56-64.57°C $D^{25°}_{4°} = 0.78646$. Water was purified in the usual way and was kept only for short periods and always in waxed vessels.

Apparatus. The polarimetric apparatus, thermostat, and temperature control were similar to those previously described by one of us[1] and the source of illumination was a Cooper Hewitt mercury arc lamp. In order to minimise surface action, the polarimeter tubes were waxed before each experiment with purified paraffin wax dissolved in petroleum ether. In carrying out the determination of the velocity of mutarotation there was generally a considerable unavoidable interval after adding the sugar to the solvent before a reading could be taken. This was chiefly due to the time required for the solution of the glucose in mixtures rich in methyl alcohol. The determinations were all carried out at 25°C.

Experimental Results

The velocity of mutarotation of glucose in methyl alcohol alone varied considerably in different determinations although the procedure was apparently the same. No explanation for this variation has yet been found, but it is apparently due to varying contamination by traces of impurity. The velocity constant obtained was in all cases considerably lower than values recorded by other investigators. In several cases, there was a distinct lag at the beginning, during which the velocity of mutarotation was almost or entirely arrested, similar to the lag recently observed by Lowry and Richards[2]. In one experiment, the velocity constant was exceptionally low, due possibly to a prolongation of the period of lag observed in other experiments. Subsequent attempts have failed to reproduce this low value. The details of this experiment are given in Table I.

A slight temporary rise of temperature occurred shortly after the experiment had proceeded thirteen hours. Observations were continued for another ten hours and the mean velocity constant for the latter part of the experiment was found to be the same as above, viz. 0.000030.

In other experiments the values obtained were 0.0_333, 0.0_344, 0.0_339, 0.0_387, 0.0_345, 0.0_331.

The lowest values previously recorded are those of Lowry and Richards at 20° viz. 0.0008 and 0.0006. Baker, Ingold and Thorpe, working at 44.8°, found K = 0.00275 calculated on the same basis. Taking into account the difference in temperature our lowest value is about twenty-five times smaller than previous values, suggesting the possibility of still lower or even zero values being arrived at under ideal conditions.

[1] Worley: Proc. Roy. Soc., **87** A, 563 (1912).
[2] J. Chem. Soc., **127**, 1394 (1925).

The velocity of mutarotation of α glucose in water has been measured by Osaka[1], Hudson[2], Kuhn and Jacob[3] and others. Kuhn and Jacob obtained a velocity of 0.0104 and Osaka and Hudson each obtained 0.0096. In three determinations we obtained the following values 0.00957, 0.00956, 0.00950 closely agreeing with the value obtained by Osaka and Hudson.

The velocity of mutarotation in mixtures of methyl alcohol and water in proportions varying from 0 to 100 per cent water are given in Table II, the proportions being expressed as molecular percentages. The results are shown

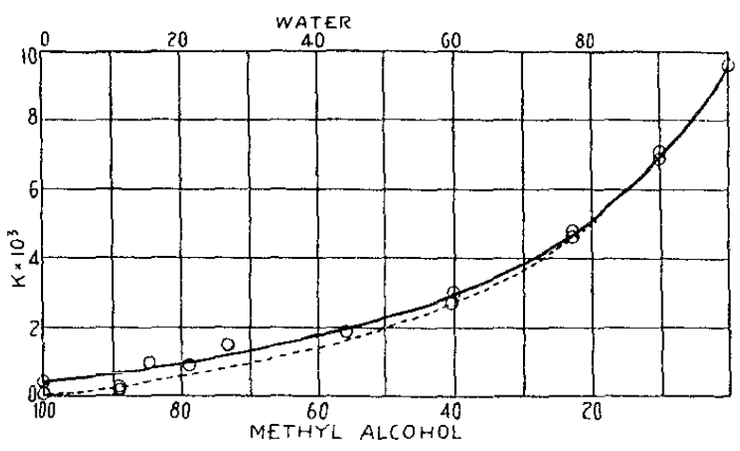


FIG. 1

graphically in the accompanying curve (Fig. 1) in which the velocity constants are plotted as ordinates and the molecular percentages of water and methyl alcohol as abscissae.

TABLE I

Methyl Alcohol 100 mols. α glucose 0.1806 mols.
$D.^{25°}_{4°} = 0.79312$. T = 25°C. Interval before first reading 40 min.

$$K = \frac{1}{t_2 - t_1} \log_{10} \frac{a - x_1}{a - x_2} \qquad t_2 - t_1 = 360 \text{ min.}$$

Time (hrs)	Observed Rotation		K
0	2.080		—
1	2.078		—
2	2.074		—
3	2.071		0.0_4 28
4	2.068		30
5	2.064		31
6	2.060		30
7	2.056		31
8	2.052		31
9	2.050		29
10	2.046		29
11	2.042	Mean	0.000030
12	2.040		
13	2.036		

[1]Z. physik. Chem., **35**,663 (1900).
[2]J. Am. Chem., Soc., **29**, 1571 (1907).
[3]Z. physik. Chem., **113**, 387 (1924).

TABLE II

Molecular Percentage CH_3OH	Molecular Percentage H_2O	$K \times 10^3$
100	0	0.4 (mean)
		0.03 (minimum)
89.0	11.0	(1) 0.2
		(2) 0.3
84.8	15.2	1.0
87.7	21.3	0.9
73.4	26.6	1.5
55.8	44.2	1.9
40.4	59.6	2.7
40.1	59.9	3.0
22.8	77.2	(1) 4.6
		(2) 4.8
10.0	90.0	(1) 6.9
		(2) 7.1
0	100	9.6 (mean)

It should be remarked that the low values of K at a concentration of 89 per cent methyl alcohol were obtained at about the same time as the lowest value of K for methyl alcohol alone, viz. 0.0_43. Since the lowest values at any concentration are probably obtained when the experimental conditions are most satisfactory extra weight should be given to low values. In the figure the full curve is drawn giving equal weight to all values while the dotted curve is drawn through points representing the minimum values obtained. From the curve it is seen that within the limits of experimental error the velocity constants lie on a smooth curve, and also that the effect of the addition of methyl alcohol to water has a much greater effect in decreasing the velocity than the addition of water to methyl alcohol has in increasing the velocity of mutarotation.

The comparatively small effect of the addition of small amounts of water to methyl alcohol is in accordance with the results of determinations made by Baker, Ingold and Thorpe. We do not, however, interpret the experimental results in the same way, but are leaving the discussion of the mechanism of the process till a later communication after more experimental data have been obtained.

Summary

1. The velocity of mutarotation of α glucose in methyl alcohol, water and mixtures of methyl alcohol and water has been determined at 25°C.

2. The value of the velocity constant obtained in the case of water was approximately the same as the lowest value previously recorded.

3. In the case of methyl alcohol a much lower value was obtained than any recorded by previous investigators.

4. The velocity constants obtained in mixtures of methyl alcohol and water lie on a smooth curve.

5. Addition of small amounts of methyl alcohol to water has a much greater effect in reducing the rate of mutarotation than the addition of water to methyl alcohol has in increasing the rate.

We have to acknowledge our indebtedness to the Royal Society for a grant to one of us (F. P. W.) towards the cost of polarimetric apparatus, and to the Duffus Lubecki Scholarship Fund for a Scholarship which enabled one of us (J. C. A.) to take part in this investigation.

Auckland University College,
University of New Zealand,
December 20, 1926.

THE ABSOLUTE ZERO OF THE EXTERNALLY CONTROLLABLE ENTROPY AND INTERNAL ENERGY OF A SUBSTANCE OR MIXTURE

BY R. D. KLEEMAN

The properties of the internal energy and entropy of a substance at the absolute zero of temperature and the connection of these properties with those at higher temperatures has recently attracted a considerable amount of attention, and given rise to a good deal of experimental research. The importance of the subject was probably first recognized by Nernst who enunciated his well known heat theorem in this connection. The development of the subject ultimately resulted in a theorem which is often called the third law of thermodynamics. The object of this paper is to show that these results are only cases of a much more general result, which can be deduced directly from results of an axiomatic character.

1. *The Division of the Internal Energy and Entropy into Two Parts.*

The internal energy of a substance or mixture of given mass may be divided into two parts, one of which is a function of the variables temperature and volume only, while the remaining part is independent of these quantities. The first part will accordingly be externally controllable while this will not be the case with the other part, and hence these two parts will be called the externally controllable and externally uncontrollable internal energy of the system. The heat absorbed when the temperature of a substance is increased, or its volume is isothermally increased, are examples of changes in the controllable internal energy of a system. Changes in the uncontrollable internal energy would evidently be spontaneous. An example of such a change is the ejection of α and β rays during radio-active changes, for these changes are independent of temperature and volume, and therefore take place spontaneously. The liberated energy in such a case, however, becomes controllable internal energy. It would be interesting to know if the reverse may happen.

Similarly the entropy of a substance or mixture may be divided into two parts, one of which is externally controllable while the other is not.

In speaking of the thermodynamical equilibrium of a system, such as a mixture in a number of phases, it is tacitly assumed that the nature of the equilibrium will not change unless made to do so from the outside by a change in temperature, volume, or masses of some of the constituents. The equilibrium therefore depends upon the controllable internal energy and entropy of the system. Similarly, any reversible process in thermodynamics is externally controllable, and therefore involves changes only in the controllable internal energy and entropy. These particular quantities are therefore of great thermodynamical importance.

If u denote the controllable internal energy of a mass of matter we may accordingly write

$$\mathrm{u} = \psi_{\mathrm{u}}(\mathrm{T}, \mathrm{v}, \mathrm{M_a}, \mathrm{M_b}, \ldots .) \qquad (1)$$

where v denotes the volume of the matter at the absolute temperature T, and $\mathrm{M_a}$, $\mathrm{M_b}$, ... denote the masses in gram atoms of the constituent $a, b, \ldots$. Similarly if S denotes the controllable entropy we may write

$$\mathrm{S} = \psi_{\mathrm{s}}(\mathrm{T}, \mathrm{v}, \mathrm{M_{,a}}\, \mathrm{M_b}, \ldots .) \qquad (2)$$

Since u by definition is the controllable internal energy it will have a zero value for certain values of v and T. For if this were not so let $\mathrm{u_1}$ denote the least possible value u can have. Now the internal energy $\mathrm{u_1}$ could not be externally controlled, or its value reduced by changes in the values of v and T, and therefore it does not consist of controllable internal energy. The values of v and T corresponding to a minimum of u would therefore give a zero value to the controllable internal energy.

Similarly it can be shown that the controllable entropy is zero corresponding to its minimum value for certain values of v and T.

If a surface is plotted with v, T, and u as axes, u being taken in its general sense, it will be evident that the zero of the controllable internal energy corresponds to a point where a plane parallel to the v and T axes touches the surface. Similarly in the case of a surface with v, T, and S as axes, the zero of controllable entropy corresponds to the point where a plane parallel to the v and T axes touches the surface. The zero of the controllable internal energy and entropy may definitely be determined, the reasoning depending in the main on the following theorem:—

2. *The Specific Heat* $\left(\frac{\partial u}{\partial T}\right)_v$ *at Constant Volume of a Substance or Mixture can have only Positive Values.*

This theorem is a direct consequence of our fundamental conceptions of heat and temperature, according to which an increase of temperature of a mass of matter kept at constant volume is associated with an increase in the heat content. It can therefore be shown to be intimately connected with the laws of thermodynamics. As is well known the thermodynamical scale of temperature is founded on Carnot's cycle. This depends on heat flowing to a substance or mixture on expanding it isothermally and on its temperature decreasing on expanding it adiabatically. It may be remarked that it is one of our fundamental experiences with matter that its temperature may be decreased to any desired extent by adiabatically decreasing its volume sufficiently. Under these conditions only can the heat taken in at the higher temperature during the cycle be larger than the heat given out at the lower temperature, the difference representing the external work done, as is demanded by the laws of thermodynamics. It follows also from these laws that the amount of work obtained is independent of the nature of the substance or mixture used, provided we work between the same temperature limits and the same amount of heat disappears as such, on which considerations the absolute temperature scale is based.

Now suppose that a mass of matter has its temperature increased from T_1 to T_2 at constant volume, giving rise to a algebraical increase in entropy equal to $\sum \int_{T_1}^{T_2} \frac{C_v}{T} \cdot \partial T$, where C_v denotes the specific heat at constant volume. Next suppose that the volume is adiabatically increased till the temperature has fallen to T_1. Lastly suppose that the volume of the matter is isothermally decreased till it regains its initial value, during which a quantity of heat Q is given out, and a corresponding decrease Q/T_1 in entropy takes place. This decrease is equal to the foregoing increase, and hence

$$\sum \int_{T_1}^{T_2} \frac{C_v}{T} \cdot \partial T = \frac{Q}{T_1}$$

According to this equation C_v or $\left(\frac{\partial u}{\partial T}\right)_v$ is positive.

It may also be noted that since the theorem is based on the laws of thermodynamics, which are the outcome of experience, physically absurd results (in the light of our experience) would be obtained if we suppose that the theorem does not hold. Thus it is evident that if the temperature of the surrounding medium is increased by ∂T an initial flow of heat to the substance will take place, whether its specific heat is positive or negative, otherwise nothing would ultimately happen with the substance. This will be attended by an absorption of heat. It will then be found that if we suppose that the specific heat is negative it may have an indeterminate value, or the lowering or raising of the temperature of the substance over a finite range can only be carried out by periodically reversing the flow of heat. These are of course absurd results in the light of our experience.

Besides the above theorem some other results will be necessary in order to determine the zero of the controllable internal energy and entropy whose truth according to our experience is even more obvious, and which will therefore be designated as postulates.

3. *The Coefficients* $\left(\frac{\partial p}{\partial T}\right)_v, \left(\frac{\partial p^2}{\partial T^2}\right)_v$ *cannot have Infinite Values.*

Since the pressure of a substance is due to the motion of translation of the molecules, an increase in the magnitude of this motion through an increase of temperature is not likely to be attended by an infinite increase in pressure, or $\left(\frac{\partial p}{\partial T}\right)_v$ cannot have an infinite value. For the same reason $\left(\frac{\partial^2 P}{\partial^2 T}\right)_v$ cannot have an infinite value.

We shall now proceed to apply the results of this and the preceding Section.

4. *The Absolute Zero of the Controllable Internal Energy of a Mass of Matter.*

Let us consider a mass of matter in the condensed state under the pressure of its vapour at the absolute zero of temperature. It can be shown that the controllable internal energy always increases in passing from this state

to another physical possible state. Since such a change is brought about by a variation of v and T, it may be noted at the outset that the controllable internal energy only will undergo a change. Thus suppose that the matter is isothermally compressed. This can be shown to be attended by an increase in internal energy.

On multiplying the thermodynamical equation

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p \qquad (3)$$

by ∂v and integrating it between the limits v and v', u and u' we obtain

$$u - u' = \int_{v'}^{v} \left\{ T\left(\frac{\partial p}{\partial T}\right)_v - p \right\} . \partial v$$

At the absolute zero of temperature this equation becomes

$$u - u' = -\int_{v'}^{v} p \, . \, \partial v \qquad (4)$$

since $T = 0$, and $\left(\frac{\partial p}{\partial T}\right)_v$ is not infinite according to the postulates in the preceding Section. If v is taken equal to v_0, the volume of the mixture in the condensed state at the absolute zero of temperature under the pressure of its vapour, and v' is less than v_0, p is positive for values of v lying between v_0 and v' inclusive. Hence $u' - u$ is positive, or if the volume is isothermally decreased from v_0 to v' this is attended by an increase in u.

This result follows also from the fact that the atoms of a substance in the condensed state at the absolute zero of temperature are in equilibrium under their forces of attraction and repulsion. Hence when the volume is decreased repulsion is the outstanding force, and the internal energy is accordingly increased during a process of compression.

If the volume of the substance is plotted against its temperature the foregoing operation corresponds to passing from the point v_0 to the point v' in Fig. 1.

Next suppose that the substance kept at the constant volume v' has its temperature increased to T, which in Fig. 1 corresponds to passing from the point v' to the point T. This is attended by an increase in internal energy according to the theorem in Section 2. Thus the whole process, since it involves variations of v and T, gives rise to an increase in the controllable internal energy. This result will evidently apply to any point lying in the compartment in Fig. 1 made by the line $v_0 a$ and the positive axes of v and T.

Next suppose that the mass of matter in the same initial state as before, namely in the condensed state in contact with its vapour at the absolute zero of temperature, has its volume isothermally increased to v'', which corresponds to passing from the point v_0 to the point v'' in Fig. 1. The matter

would divide itself into a solid and vaporous phase. The amount of matter in the latter phase would however be zero, since the pressure is zero. The process is therefore not attended by a change in internal energy.

Since, when v'' is infinite the amount of evaporated matter may be finite, we may proceed more strictly thus: The heat absorbed, if any is absorbed, can only have a positive value according to the fundamental properties of Carnot's cycle pointed out in Section 2. Now the external work done is equal to ART, where A is a constant, and therefore zero, since T = 0. Therefore a positive increase in internal energy only can take place.

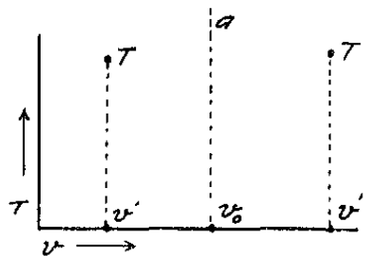


FIG. 1

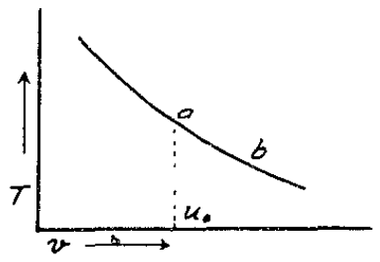


FIG. 2

Next suppose that the temperature of the matter is raised to T keeping the volume v'' constant, which corresponds to passing from the point v'' to the point T in Fig. 1. This is attended by an increase in internal energy according to the theorem in Section 2. Thus the controllable internal energy of the matter has been increased during the process. This result will evidently also apply to any point in the space in Fig. 1 to the right of the line $v_0\, a$.

It follows then that the total internal energy of the mass of matter in its initial state has a smaller value than for any other physically possible state. Therefore according to the definition of and properties of the controllable internal energy given in Section 1, its value is zero, when the matter is in the condensed state under the pressure of its vapour at the absolute zero of temperature.

We may now proceed to the consideration of the entropy.

5. *The Absolute Zero of the Controllable Entropy of a Mass of Matter*

The absolute zero of the controllable entropy according to Section 1 corresponds to the state for which it can be shown that the controllable entropy has a smaller positive value than for all other physically possible states. Such a state should exist. For suppose that the entropy is measured from a given state chosen arbitrarily. Let the state of greatest negative entropy be obtained corresponding to this state. We may then transfer the zero to the latter state and measure the entropy from this state. It would evidently correspond to the foregoing definition of the zero of controllable entropy.

Let the point u_0 on the v axis in Fig. 2 correspond to the zero of the controllable internal energy. Let the curve ab be an adiabatic corresponding to zero entropy. Now as we pass from the zero point of internal energy u_0 to the point a on the adiabatic which corresponds to the same volume, the internal energy is increased, and hence the entropy is increased. Therefore on passing from the point a to the point u_0 the entropy is decreased. But

since the adiabatic corresponds to zero entropy, the entropy should increase under these conditions. It follows therefore that the adiabatic must pass through u_o, or a substance or mixture in the condensed state in contact with its vapor at the absolute zero of temperature corresponds to a state on the adiabatic of zero entropy. We may therefore take this state to correspond to zero entropy. This zero, which is the same as that of the internal energy, will for convenience be called the absolute zero of control.

The possibility that the substance may exist in several different (crystalline) forms at the absolute zero of control which possess different internal energies and entropies, remains to be considered. Suppose that two such forms are mixed at the absolute zero of temperature. The change Δu in internal energy is given by the thermodynamical equation

$$\Delta u = T \frac{dW}{dT} - W$$

where W denotes the external work done during the process of mixing. This may be carried out by allowing both forms to evaporate, mixing the resultant gases, and condensing the mixture. It will now be clear that the work done may be expressed in the form ΔAT, where A is a constant. Hence when $T = o$ it follows from the above equation that $\Delta u = o$, or no change in internal energy takes place on mixing. Thus the two forms have the same internal energy, which is zero.

It can be shown that a similar result holds for the entropy. The change in internal energy during an adiabatic change is given by

$$\left(\frac{\partial u}{\partial v}\right)_s = - p$$

which may be written

$$\left(\frac{\partial u}{\partial v}\right)_s = \left(\frac{\partial u}{\partial v}\right)_T - T \left(\frac{\partial p}{\partial T}\right)_v$$

by means of equation (3). At the absolute zero of temperature for any state this equation becomes

$$\left(\frac{\partial u}{\partial v}\right)_s = \left(\frac{\partial u}{\partial v}\right)_T$$

It expresses that as we pass isothermally from one form of the substance to another no change in entropy takes place.[1]

Since the results of this Section are based on thermodynamics, deductions made from them will not apply to substances which cannot be passed through any conceivable thermodynamical cycle. They would therefore probably not apply to such a substance as glass, which, if evaporated and condensed again, is hardly likely to be in the same state as before, i.e., glass. A supercooled liquid probably does not admit of being passed through a cycle, at least in some cases, and to them these restrictions will therefore also apply.

[1] This proof is not quite satisfactory, but will have to suffice here. A better proof will be given in a subsequent paper.

A number of relations corresponding to the zero of control may be found by the help of the postulates of the next Section.

6. *The Differential Coefficients* $\left(\frac{\partial u}{\partial v}\right)_T$, $\left(\frac{\partial u}{\partial T}\right)_v$, *and* $\left(\frac{\partial S}{\partial v}\right)_T$, $\left(\frac{\partial S}{\partial T}\right)_v$ *are continuous for all Possible States of a Homogeneous Mass of Matter.*

An atom in a substance is in equilibrium under the influence of the forces of attraction and repulsion of the surrounding atoms. If these forces are not discontinuous for certain distances from their sources the above postulates would evidently hold. There does not seem to be any evidence whatever in nature of the existence of such discontinuities.

7. *Some Relations at the Absolute Zero of Control.*

Since the zero of internal energy corresponds to the least value it can have and $\left(\frac{\partial u}{\partial v}\right)_T$ and $\left(\frac{\partial u}{\partial T}\right)_v$ are not discontinuous, it follows from the Differential, Calculus that the zero satisfies the conditions for a minimum, and hence we will have:

$$\left(\frac{\partial u}{\partial v}\right)_T = 0 \tag{5}$$

$$\left(\frac{\partial u}{\partial T}\right)_v = 0 \tag{6}$$

$$\frac{\partial^2 u}{\partial T^2}\frac{\partial^2 u}{\partial v^2} - \left(\frac{\partial^2 u}{\partial v \,.\, \partial T}\right)^2 > 0 \tag{a}$$

$$\frac{\partial^2 u}{\partial v^2} > 0 \tag{b}$$

$$\frac{\partial^2 u}{\partial T^2} > 0 \tag{c}$$

A similar set of equations and inequalities hold for the entropy at the absolute zero of control. Since at this state the entropy has the least possible value, and $\left(\frac{\partial S}{\partial v}\right)_T$ and $\left(\frac{\partial S}{\partial T}\right)_v$ are not discontinuous according to the postulates in the preceding Section, it follows that the entropy satisfies the conditions of a minimum, and hence we have:

$$\left(\frac{\partial S}{\partial v}\right)_T = 0 \tag{7}$$

$$\left(\frac{\partial S}{\partial T}\right)_v = 0 \tag{8}$$

$$\frac{\partial S^2}{\partial T^2}\,\frac{\partial S^2}{\partial v^2} - \left(\frac{\partial^2 S}{\partial v\,.\,\partial T}\right)^2 > o \qquad (d)$$

$$\frac{\partial S^2}{\partial v^2} > o \qquad (e)$$

$$\frac{\partial^2 S}{\partial T^2} > o \qquad (f)$$

Equation (6) expresses that the specific heat of a substance or mixture in the condensed state kept at constant volume is zero at the absolute zero of temperature. This result is part of Nernst's theorem.

A formula for the specific heat of a substance in the gaseous state at infinite volume may be found which expresses an important property of this quantity. On multiplying equation (3) by ∂v and integrating it between the limits ∞ and v it becomes

$$u_\infty - u = \int_v^\infty \left\{ T \left(\frac{\partial p}{\partial T}\right)_v - p \right\} \partial v \qquad (9)$$

where u_∞ denotes the internal energy of the substances at infinite volume. Let us suppose that we are dealing with a mixture whose equation of state may be expanded in the form

$$p = \frac{ART}{v} + \frac{B}{v^\alpha} + \frac{C}{v^\beta} + \cdots$$

where A is a constant, B, C, ... functions of T, and α, β, ... positive constants whose values are greater than unity. According to our experience this is likely to be always possible. The integral in equation (9) corresponding to the upper limit would accordingly be zero. On differentiating the equation with respect to T at constant volume we have

$$C_v = C_{v\infty} + T \int \left(\frac{\partial p^2}{\partial T^2}\right)_v . \partial v \qquad (10)$$

where C_v denotes the specific heat at the volume v, and $C_{v\infty}$ that at infinite volume with the matter in the gaseous state. This equation applies to matter in any state. On applying it to a substance at the absolute zero of control the integral will not become infinite since $\left(\frac{\partial^2 p}{\partial T^2}\right)_v$ is not infinite according to the postulates in Section 3, and the volume has the finite value v_o. The integral term therefore becomes zero, since $T = o$. Since we also have $C_v = o$ the equation gives

$$C_{v\infty} = o \qquad (11)$$

or the specific heat of a gas at constant infinite volume is zero at the absolute zero of temperature.

This is an interesting and important result, and is especially striking when a non-atomic gas is considered. Evidence of its truth already exists. Scheele and Heuse[1] have measured the specific heat of helium at various temperatures and found that it decreased though slightly with decrease of temperature. Thus for example at the temperatures 18°C and −180°C the specific heats were found to have the values 3.008 and 2.949 respectively.

The explanation of the result is probably that though the atom absorbs energy on increase of temperature due to an increase in the kinetic energy of translation, energy is also given out due to internal changes in the atom. These two changes balance each other at and near the absolute zero of temperature, or if −u denotes the heat given out per gram molecule by the molecules from their internal controllable source of energy per unit increase in temperature, and 3/2 R the heat absorbed through the increase in kinetic energy of motion of translation, we would have

$$3R/2 - u = 0 \qquad (12)$$

at the absolute zero of temperature. It should be noted in this connection that the internal energy of a number of molecules in the gaseous state at the absolute zero of temperature is not zero according to Section 4.

It appears from this explanation of the specific heat of a gas at the absolute zero of temperature, that it is not necessarily associated with a deviation from the gas laws, or the gas laws may hold for all temperatures. It is not impossible of course that the correct explanation is a different one than the foregoing, though at present it seems the most plausible.

It should be mentioned that Nernst[2] has deduced a formula for the decrease of the specific heat of a gas with decrease of temperature from a given theory of the atomic model and quantum considerations.

Formulae for the controllable internal energy and entropy of a substance or mixture may immediately be deduced corresponding to the volume v and absolute temperature T. Suppose that a substance or mixture at the absolute zero of control has its temperature raised to T keeping its volume v_o constant. The change in internal energy is equal to $\int_0^T C_v, \partial T$, where C_v denotes the specific heat corresponding to the constant volume v_o. Next suppose that the volume is changed to v at constant temperature. The change in internal energy is $\int_{v_o}^{v} \partial u$. The total change in internal energy, which is the controllable internal energy u of the substance, is therefore given by

$$u = \int_0^T C_v \,.\, \partial T + \int_{v_o}^{v} \partial u \qquad (13)$$

[1] Ann. Physik, (4) **40**, 484 (1913).

[2] Ber. deutsch. physik. Ges., **18**, 85-116 (1916).

On substituting for ∂u from equation (3) and for C_v from equation (10) applied to the substance at the volume v_o, in the foregoing equation, it becomes

$$u = \int_o^T \left[C_{v\alpha} + \int T \left(\frac{\partial p}{\partial T} \right)_v \partial v \right]_{v = v_o} \partial T + \int_{v_o}^v \left\{ T \left(\frac{\partial p}{\partial T} \right)_v - p \right\} \partial v \qquad (14)$$

The expression for the entropy S obtained along the same lines is given by

$$S = \int_o^T \left[\frac{C_{v\alpha}}{T} + \int \left(\frac{\partial p}{\partial T} \right)_v \partial v \right]_{v = v_o} \partial T + \int_{v_o}^v \left(\frac{\partial p}{\partial T} \right)_v \partial v \qquad (15)$$

The value of v_o is given by

$$v_o = 2.6 \, \Sigma \, N_w \sqrt{a_w} \qquad (16)$$

according to Traube[1], where N_w denotes the number of gram atoms of atoms of atomic weight a_w relative to the hydrogen atom the substance contains. Thus if the equation of state of the substance or mixture and the specific heat $C_{v\alpha}$ be known the controllable internal energy and entropy may immediately be evaluated. Any empirical equation of state may be used provided its constants are determined from the facts. The controllable free energy F and the controllable thermodynamical potential Φ may then be obtained from the equations

$$F = u - TS \qquad (17)$$

$$\Phi = u - TS + pv \qquad (18)$$

It will be found that in all thermodynamical formulae useful for calculation we may substitute the controllable internal energy, entropy, free energy, and potential since the uncontrollable parts would disappear through differentiation or otherwise.

A number of other important formulae may be derived which will be given in a subsequent paper.

[1] Physik. Z., 1909, 667.

THE SYSTEM WATER-PHENOL*

BY JOHN BRIGHT FERGUSON[1]

The system water-phenol is frequently cited as an example of a system in which two liquid phases occur. Such systems are of unusual interest since they provide a knotty problem for the proponents of the various theories which deal with "Solubility". The data dealing with such systems are unfortunately not very extensive and we have therefore endeavoured to supplement it by a number of calorimetric and vapour pressure measurements. The results of our experimental work together with a discussion of the available data are given in the following paper.

Part I. Specific Heats

The materials employed were distilled water and redistilled, Kahlbaum's synthetic C. P. phenol, melting point[2] 40.8°C. The solutions were made up by weight. The calorimeter proper consisted of a 250 cc small-mouth Dewar flask. It contained a glass-enclosed constantan-wire electric heater which had a resistance of 26,07 ohms, one end of a glass-enclosed, twelve-junction copper-constantan thermel and a rotary stirrer. The top of the flask was fitted with a rubber stopper which in turn fitted tightly the cases of the heater and thermometer and also the long glass bearing of the stirrer. The bearing was sealed and lubricated by a special very heavy rubber lubricant. The flask stood in a well-controlled air bath which in turn was inside a larger air bath. A similar Dewar flask was immersed in a water thermostat which was placed in the larger air bath. This flask contained the cold junctions of the calorimetric thermometer and one end of a reference thermometer of six junctions the other end of which was placed in an ice bath. This cold junction flask was provided with a rubber stopper having four holes. Two of these were for the cases of the thermometers and the other two for removable glass plugs. When these plugs were removed, a pipette was inserted in one hole and the bath water drawn into the flask. The flask contained no stirring device but all the available space was filled with strips of copper foil which extended the length of the flask.

The thermels were calibrated at the following points:

(a) B. P. water.

(b) Tr.[3] $SrCl_26H_2O$, 61,341°C.

(c) Tr.[4] $Na_2SO_410H_2O$, 32,384°C.

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* Contribution from the Department of Chemistry, University of Toronto.

[1] For preliminary reports see Ferguson: Trans. Roy. Soc. Can., (3), **17**, 160 (1923); Ferguson and Funnell: **18**, 122-3; Ferguson and Hope: 121 (1924).

[2] The melting point was determined with a thermel.

[3] Richards and Yngve: J. Am. Chem. Soc., **40**, 89 (1918).

[4] Dickenson and Mueller: J. Am. Chem. Soc., **29**, 1381 (1907).

The heating current was obtained from a set of storage batteries. A precision potentiometer was used both to measure the temperatures and also to check the heating current by determining the drop of potential across a known resistance.

With attention to details, the reference temperature bath was found satisfactory. In one case, two hours after changing the water, the bath temperature fell 0,0033°C in ten minutes. The change of temperature was in all cases regular and could be followed by means of the reference thermometer. The actual temperature of the reference bath was adjusted so that in any experiment it was just below the lowest temperature attained by the calorimeter.

The cooling or heating corrections were from 3 to 4 percent of the total heat supplied in experiments in which the actual heating took place in about 10 minutes. The calorimeter was calibrated using distilled water and in two experiments with cooling corrections, values of 14,76 and 14,96 cal. were obtained. An experiment in which a heating correction was necessary gave a value of 14,47 cal. The value of 14,73 cal. was used for the temperature interval 70° to 74°C. The heat usually supplied was 320 cal.

The results of these experiments[1] are given in Table I.

TABLE I

The Mean Specific Heats of Water-Phenol Solutions for the Temperature Interval 70° to 74°

Composition Wt. percent Phenol	Temperature Interval Deg. C.	Specific Heat calories*
0,00		1,001 (assumed value)
20,04	1,746	0,9350
	1,741	0,9396
40,15	1,823	0,8640
	1,660	0,8648
60,02	2,018	0,7597
	1,833	0,7633
79,9	2,105	0,6545
100,0	2,117	0,5486
	1,782	0,5487

* *1 calorie = 4,182 joules.*

These results show a slight positive deviation from a straight line relationship and the point of maximum deviation is, approximately, at the consolute composition.

The specific heat of phenol has been previously determined by Schlamp[2] who obtained a value of 0,561 for the temperature 93.9°C.

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[1] In the summary of this work previously reported, the composition 20,04 wt. percent phenol was erroneously given as 23,04 percent.

[2] Schlamp: Ber. oberhess. Ges. f. Nat. u Heilk., **31**, 100 (1895).

Part II. The Heats of Mixing

The apparatus described in the preceding section was in the main used in the following experiments. A new calorimeter was however necessary. The one liquid was placed in a Dewar flask and the other liquid in a glass container which was immersed in the first liquid when in use. Stirring was obtained by rotating the glass container. The mixing occurred when two glass plugs were removed from openings in this container. One opening was

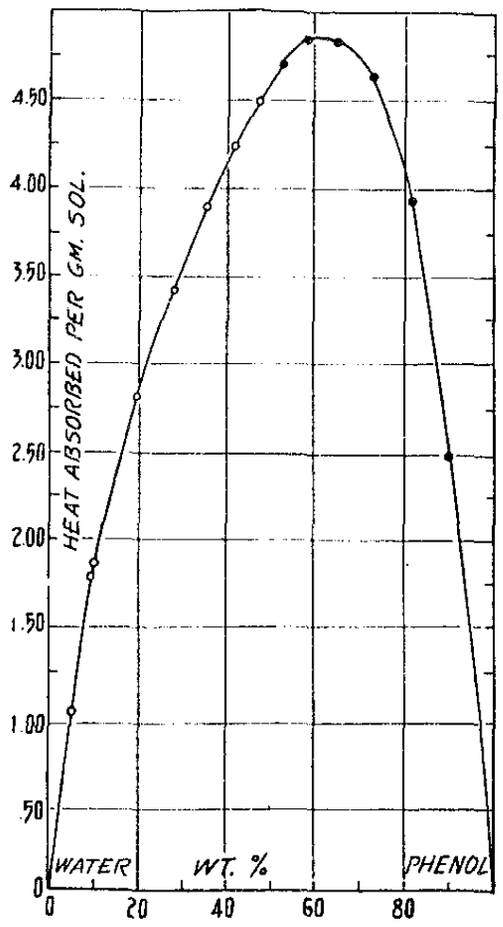


FIG. 1
The heat absorbed in the formation of water-phenol solutions at 71° C.

at the bottom centre and the other at the top on one side. When the plugs were removed the rotation gave rise to complete mixing due in part to centrifugal action. The heat capacity of this calorimeter was 26,05 ± 0,4 cal. The cooling or heating corrections were about one percent of the total heat quantity in most of the experiments. The volume capacity of the inner container was 25 cc so that differential measurements were necessary. Two series of experiments were carried out. In one series, the water was added to the phenol or to a solution and in the other the phenol was added to water or a solution. The results of these experiments, which were carried out at approximately 71°C and calculated to this temperature, are given in Table II and a graph of them is shown in Fig. 1.

TABLE II

The Heat absorbed in the Formation of one Gram of Solution from the pure Constituents at 71°C.

Experimental Series	Composition Wt. Percent Phenol	Heat absorbed 15° calories
A	5,17	1,012
	9,73	1,794
	10,23	1,867
	19,75	2,818
	28,06	3,420
	35,57	3,898
	41,86	4,240
	47,28	4,499
B	52,70	4,706
	58,37	4,850
	64,78	4,836
	72,85	4,643
	80,95	3,934
	90,10	2,478

Part III. Vapour Tension Measurements

Schreinemakers[1] has determined the vapour pressures of solutions of phenol and water. His values are unfortunately not very exact. Our own experiments were designed primarily to check certain of his results.

The tensimeter consisted of two glass bulbs connected by a U tube which contained mercury. When in use the bulbs were immersed in a water bath and the emergent glass tubes were heated electrically to prevent condensation. The chief difficulty encountered was that of freeing the liquids of air. This was accomplished by heating the liquids above the critical temperature between evacuations and shaking violently. We could not remove the air from the phenol rich layer at room temperature by repeated evacuations and agitation in any reasonable time. After each experiment the solutions were analysed using Lloyd's method.[2] Water was used as an initial reference material and for it a vapour pressure of 289,1 mm was assumed.

Our results are given in Table III.

Especial care was taken with the differential measurements of the 23,33 and 46,81 percent solutions. There can be no question but that the vapour tensions of these solutions do not differ by more than 0,2 mm. Our results confirm the earlier work of Schreinemakers though the actual pressure given by him for these solutions is 294 mm.

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[1] Schreinemakers: Z. physik. Chem., **35**, 464 (1900).

[2] Lloyd: J. Am. Chem. Soc., **27**, 16 (1905); Redman and Rhodes: J. Ind. Eng. Chem., **4**, 655 (1912).

TABLE III

The Vapour Tensions of Water-Phenol Solutions at 75°C.

Composition Wt. percent Phenol	Vapour Tension Millimeters Mercury	Composition Wt. percent Phenol	Vapour Tension Millimeters Mercury
0	289,1	46,81	290,1
7,19	290,5		290,1
	290,4		290,2
	290,5	59,76	289,1
	290,5		289,2
23,33	290,2		289,25

Part IV. Thermodynamics[1]

The unaccented symbols refer to a liquid phase at a temperature θ deg. K. and at atmospheric pressure while the accented symbols refer to the same phase at the same pressure but at a new temperature θ'. The specific heats are assumed to be independent of the temperature.

$$\bar{z} = \bar{x} - \theta\bar{\eta}$$

$$\bar{z}' = x' - \theta'\bar{\eta}' = \bar{x} - \bar{c}\,(\theta - \theta') - \theta'\left(\bar{\eta} - c \log_E \frac{\theta}{\theta'}\right)$$

Hence:—

$$\bar{z}' = \frac{\theta'}{\theta}\bar{z} + \frac{\theta - \theta'}{\theta}\bar{x} - \bar{c}\left\{(\theta - \theta') - \theta' \log_E \frac{\theta}{\theta'}\right) \qquad \text{I}$$

and

$$\frac{D^2\bar{z}'}{Dx^2} = \frac{\theta'}{\theta}\frac{D^2z}{Dx^2} + \frac{\theta - \theta'}{\theta}\frac{D^2\bar{x}}{Dx^2} - \left\{\theta - \theta' - \theta' \log_E \frac{\theta}{\theta'}\right\}\frac{D^2\bar{c}}{Dx^2} \qquad \text{II}$$

Equation I defines the zeta for one temperature in terms of the zeta and chi for another temperature, the specific heat and the two temperatures. If we restrict this equation to systems of two components, x and y, and differentiate twice in respect to x, $(x+y=1)$, we obtain equation II. The first term of this equation is positive for all stable phases, negative for all unstable phases and zero for critical phases.

For the system water-phenol we can evaluate the first and second terms of equation II from the thermal data alone if we restrict ourselves to the consolute composition. The latter is approximately 34 wt. percent phenol and the consolute temperature[2] for *pure* phenol and water is 339 deg. K. For term two (344.1 deg. K), we obtain 0.1022 and for term one (338.1 and 333.1 deg. K) respectively −0.0085 and −0.0054. The positive sign for the stable phase is certainly established but the negative signs, while obtained, are somewhat uncertain owing to the size of the quantities involved. However if one could find a similar system in which the last two terms have the same numerical sign, the negative sign for the unstable phase would be established without a numerical calculation.

[1] For a discussion of symbols, see W. Lash Miller: Chem. Rev., **1**, 294 (1924-5).

[2] Hill and Malisoff: J. Am. Chem. Soc., **48**, 922 (1926).

From equation II, the tendency for any solution to split into two layers on changing the temperature is a function of the zeta and chi of the stable solution and of the specific heats. The function is however such that this change is unlikely when the zeta curve for the stable solutions at a temperature which is near their respective dissolution temperatures deviates much from a straight line. For the simple case in which the vapour may be considered as a perfect gaseous solution this statement may be interpreted in terms of the total and partial pressures in the following manner. The zeta for a liquid containing one formula weight of the components is given by the equation:

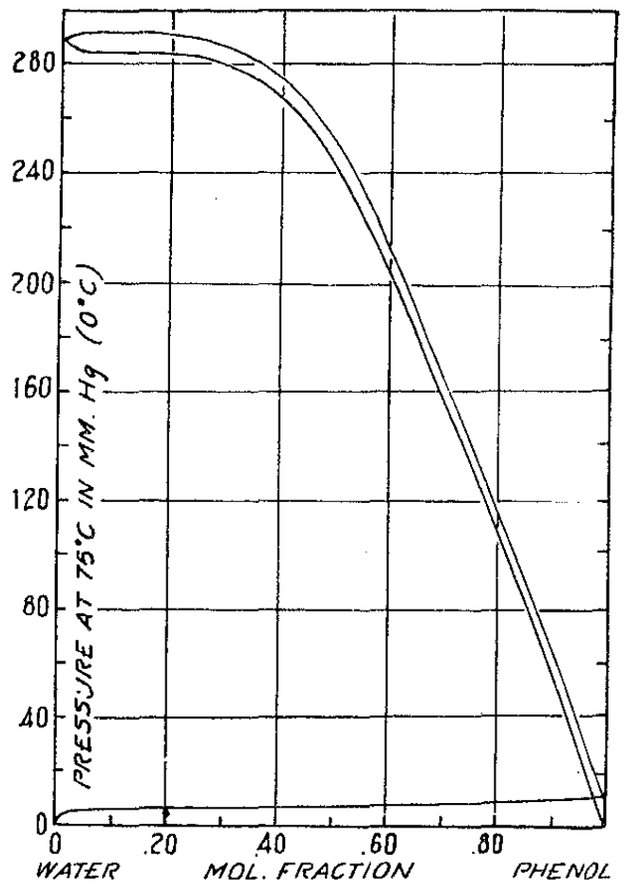


FIG. 2
The partial and total vapour pressures of water-phenol solutions at 75° C.

$$z = R\,\theta + n_1\,R\,\theta \log_E \frac{\pi_1}{p_1} + n_2\,R\,\theta \log_E \frac{\pi_2}{p_2} \qquad (n_1+n_2=1) \qquad \text{III}$$

in which R is the gas constant, θ the temperature deg. K., π_1 and π_2 the partial vapour pressures and p_1 and p_2 the vapour pressures of the components in the reference states. In each case the reference state is taken as the saturated vapour of the component at θ deg. K. and for these states ϵ and η are given zero values. If this equation be differentiated, keeping in mind the approximate equation of Duhem-Margules, we obtain

$$\frac{D^2z}{Dn_1^2} = \frac{R\theta}{n_2} \cdot \frac{1}{\pi_1} \cdot \frac{D\pi_1}{Dn_1} \qquad \text{IV}$$

from which it follows that for the zeta curve to approximate a straight line the partial pressure curve for the one component must have a nearly horizontal position parallel to the composition axis.[1] The total pressure will also have a similar curve.

These relations are approximately obeyed by the system under discussion as shown by Fig. 2. The partial pressures were calculated from the results of Scheinemakers and ourselves on the solutions and the work of Kahlbaum[2] on pure phenol, upon the assumption that the vapours were perfect gases. The consolute composition is approximately nine mols percent phenol.

For the very dilute solutions of phenol the partial pressure for water appears to obey Raoult's Law. The maximum deviation occurs at about 40 mols percent phenol and this is the approximate composition showing the maximum heat of mixing. On plotting the differential heats of mixing obtained by the method of intercepts, the curve for water is convex toward the composition axis as it approaches its origin which is in agreement with the partial pressures of the dilute solutions.

In conclusion, we wish to thank Prof. Lash Miller, Prof. W. S. Funnell and Mr. H. B. Hope for their assistance.

Summary

1. The specific heats of solutions of phenol and water have been determined at 70-74 deg. C.

2. The heats of formation of these solutions have been measured at approximately 71 deg. C.

3. The vapour tensions of a limited number of solutions were observed at 75 deg. C.

4. A thermodynamical study of the available data has been made.

Toronto, Canada.
January 10, 1927.

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[1] Although equation II is on a "one-gram basis" while equation IV is on a one formula weight basis, this does not materially affect the conclusion.

[2] Kahlbaum: Z. physik. Chem., **26**, 604 (1898).

THE LIGHT-SCATTERING CAPACITY (TYNDALL EFFECT) AND COLLOIDAL BEHAVIOUR OF GELATIN SOLS AND GELS*

BY ELMER O. KRAEMER** AND STEPHEN T. DEXTER***

One of the characteristic properties of disperse or colloidal systems is the Faraday-Tyndall effect, i.e., the capacity of such systems, when illuminated unilaterally, to scatter light in all directions. According to Rayleigh, the relative intensity of the light scattered at right angles to the axis of illumination by dilute sols of constant volume concentration, containing very small non-conducting particles, is given by the equation

$$I = \frac{kv}{\lambda 4}\left(\frac{n_1^2 - n^2}{n_1^2 + 2n^2}\right)^2$$

in which k is a constant of proportionality; v, the mean volume of the particles; λ, the wave length of the light used; and n_1 and n are the indices of refraction of disperse phase and medium respectively. With a given system, for which n_1 and n are constant, the intensity of the tyndall effect is directly proportional to the mean volume of the particles. The condition and changes of dispersion of a system are therefore directly revealed in the tyndall effect.

Very little attention has thus far been given to the significance of this property in connection with the problems associated with the colloidal behaviour of the proteins. Qualitative observations, it is true, have been made of superficial turbidities. The most important of these for gelatin systems are due to Dhéré and Gorgolewski[1] who noted the great increase in turbidity or opacity of gelatin sols as the ash content was decreased. Using purified and de-ashed gelatin in dilute systems, they described the disappearance of the turbidity above 30°C and observed the very small concentrations of acids or bases sufficient to remove the turbidity at temperatures below 30°C. Neutral salts were found to be relatively much less effective for this purpose. They first clearly described the increase in turbidity to a maximum and subsequent decrease as the concentration of the gelatin gels increased. The maximum turbidity was found to occur at approximately 2.5 percent; 10 percent gelatin gels were as free from superficial turbidity as 0.5 to 1 percent systems. At low temperatures, they further observed that the gelatin tended to precipitate out from dilute systems. These studies were probably the first to be made upon highly de-ashed gelatin (less than 0.1 percent ash).

Somewhat later, Arisz[2] recorded photographically the tyndall effects of gelatin systems in a mixed glycerine-water solvent. In spite of the complications due to ash content and mixed solvent, Arisz observed much the same

* Contribution from the Colloid Laboratory, University of Wisconsin.

** Fellow of the National Research Council during the first part of this investigation.

*** The experimental work of this paper constituted a portion of the junior author's thesis for the M.S. degree in 1925.

[1] Dhéré and Gorgolewski: J. physiol. path. gen., **12**, 645 (1910); **13**, 157, 167 (1911).

[2] Arisz: Proc. Acad. Sci. Amsterdam, **26**, 331 (1913); Kolloidchem. Beihefte, **7**, 22 (1915).

behaviour as Dhéré and Gorgolewski had recorded. Subsequent workers, in increasing number, have confirmed in a qualitative way the earlier observations on the influence of acids, bases, temperature, gelatin concentration, and purity upon the turbidity of aqueous gelatin systems. As the theory of ampholytes was applied to the behaviour of proteins in aqueous systems, the maximum turbidity became identified with the "isoelectric point," and was used in determining the H ion activity associated with this state.

The first investigation, however, of the colloidal behaviour of aqueous gelatin systems under various conditions by means of *quantitative* studies of the light-scattering capacity appeared but recently. In a paper on the optical activity of gelatin systems[1], the present authors gave a curve showing the relationship at 24°C between relative intensity of scattered light and the pH of one percent de-ashed gelatin systems. It was found that a sharp rise in tyndall intensity took place at the isoelectric point, quantitatively confirming the observations of Dhéré. Within a fraction of a pH unit, the increase exceeded 1000 percent. The maximum intensity located the isoelectric point with greater certainty and exactness than perhaps any other property of the system. About the same time, a similar curve, but inadequately defined, was published by Vlès and Vellinger.[2] On account of the paucity of data, their curve did not show the abrupt rise in tyndall effect described above.

The application of this technic to aqueous gelatin systems has been continued. Upon the assumption that the maximum tyndall intensity locates the isoelectric point, an examination of gelatins of various sources has shown that the isoelectric points do not fall at a constant pH for all gelatins. For certain bone gelatins, values as high as pH 5.5 were found. This fluctuation in isoelectric point suggests either that "gelatin" consists of an unknown number of unknown chemical entities or that the isoelectric point of such material does not bear the relation to the chemical character of the material which is implied in the application of the theory of ampholytes to its behaviour. The first alternative seems fairly well established; the second is possible. Mixed gelatins, however, do not reveal themselves as such in the tyndall effect studies. It is probable that the differences in gelatins reflect differences in the gelatin precursors.

The light-scattering capacity and its dependence on pH and temperature is of significance in connection with questions concerning the condition of gelatin in the sol state. The new data suggest that the effectiveness of a trace of acid or base in preventing precipitation of gelatin from dilute systems near the isoelectric point is probably not simply a question of protective action due to electrical charge, for the actual cataphoretic mobility is known to remain undetectable with such small electrolyte concentrations. Nor is there any immediate way by which the effect of acids and bases on tyndall effect—and by inference, on degree of dispersion—may be quantitatively interpreted in terms of the theory of ampholyte solubility as it now stands. On the other

[1] Kraemer and Fanselow: J. Phys. Chem., **29**, 1169 (1925).
[2] Vlès and Vellinger: Compt. rend., **181**, 1189 (1925).

hand, the dispersion of gelatin by increasing temperatures, as revealed in terms of light-scattering capacity, does not so much resemble an increase in true solubility of a phase of constant composition in contact with its saturated solution. Rather, the process has features in common either with conjugate solutions passing the consolute temperature, or with disperse systems passing a critical peptization temperature. The elucidation of gelatin behaviour near the isoelectric point depends upon a proper recognition and evaluation of those phenomena describable in terms of chemical reactions and compounds, and of those commonly considered characteristic of colloidal or disperse systems. It is hoped that some of the vagueness and uncertainty now present will be removed upon completion of investigations concerning salt effects and light-scattering capacity.

Procedure

The relative light-scattering capacities of the gelatin sols and gels were measured by means of an improvised tyndallimeter. A beam of light from a 6 volt, 108 watt concentrated filament source was passed through a long column of water to remove heat rays, and split into two beams by a clear glass reflector. One beam passed through a series of apertures and illuminated the gelatin systems contained in 2 oz. square medicine bottles selected for uniformity. The light scattered by the gelatin at an angle of 90° to the axis of illumination, and the reflected portion of the original beam, after passing through neutral or colored screens, slits and two nicol prisms, were brought into juxtaposition for comparison by a Lummer-Brodhun photometric head. By means of appropriately chosen screens of known transmissions in the two beams and a proper rotation of one of the nicols, the relative intensity of the scattered light was determined in terms of the intensity of the illuminating beam.

The gelatins used were of various types and grades. As specified in each case, some were commercial gelatins containing ash, others were de-ashed by various processes. The gelatin sols were prepared in a uniform fashion. A stock solution sufficient in quantity for an entire series of observations was prepared in a concentration somewhat greater than that desired in the final samples by heating appropriate amounts of swollen gelatin and water at 60°C. for 20 minutes. To measured portions of this stock, appropriate quantities of water, dilute sodium hydroxide, or dilute hydrochloric acid were added to give sols of the desired pH with one gram of vacuum-dried gelatin in 100 cc of solution at 25°C. These specimens were kept at 60°C for 20 minutes to efface any effects of previous thermal history, and then transferred to the thermostat at the temperature of which the tyndall effect was to be observed. A trace of thymol, which produced no measurable effect upon the intensities of the scattered light, was commonly used as a preservative. H ion activities were determined with the H electrode and calomel cell chain at room temperatures, and confirmed by comparison with standard buffers.

The relative intensities of the scattered light were determined after constant values were attained at a given temperature. At temperatures of

30°C and higher, a constant intensity was attained practically as soon as thermal equilibrium. Between 17° and 30°C measurements were made after 24 hours; in the absence of salts, no further appreciable change was observed during the next 50 hours.

Isoelectric Points of Gelatins

In the application of the theory of ampholytes to protein behaviour, the pH of minimum solubility or maximum precipitation tendency in the absence of salts is said to locate the isoelectric point. This point, in the case of gelatin, may be located accurately and conveniently by determining the pH of maximum intensity of scattered light. The results of applying this method to a number of specimens of de-ashed and commercial gelatins follow.

De-ashed Gelatins: A comparison of the pH's starred with those in italics indicates that only those gelatins were in the isoelectric condition which had been electrodialyzed in the gel state. The other gelatins (Eastman A, B, C, and ossein gelatin) all contained excess of acid or base. However, as shown by a comparison of Eastman A and A′, removal of the excess acid did not change the pH of maximum intensity of the scattered light, but did increase the height and sharpness of the maximum. The same constancy in the position of maximum intensity was shown by the "Silver Label de-ashed" of Table I and the original gelatin containing 1.5 percent ash. Low temperature electrodialysis as a de-ashing procedure therefore appeared to be without influence upon the isoelectric point of the gelatin; nor did the normal ash content in these cases cause any displacement of the pH of maximum intensity.

For the first five (hide) gelatins, the maximum intensity, and therefore presumably the isoelectric point, was located at practically a constant pH, 4.95-5.01, in spite of considerable differences in gel strength. For example, Eastman A and Eastman C showed essentially identical light-scattering capacities and identical isoelectric points. On the other hand, Eastman A formed stable gels at quite low concentrations, while Eastman C had the properties rather of a low grade gelatin. The data of the table demonstrate how sharply the maxima were located. It is, at the same time, evident that there is a distinct discrepancy between the position of the isoelectric points of these specimens and the value usually quoted for gelatin (pH 4.65-4.70).

A still greater discrepancy is furnished by the ossein gelatin I with its maximum light-scattering capacity and apparent isoelectric point at pH 5.5, i.e., at a H ion activity *less than one-third* as great as at the isoelectric points of the hide gelatins. It is also to be noted that the maximum was broader and flatter than was found with the hide gelatins. However, a third extraction of the ossein (ossein III) displayed a maximum intensity of scattered light near pH 4.9, with the hide gelatins. The maximum for ossein III was less abrupt and much less lofty than were the maxima for the hide gelatins. These variations and lack of uniqueness in gelatin behaviour are illustrated in greater detail by the observations on commercial gelatins which follow.

Commercial Hide and Bone Gelatins: Since, as was indicated above, the presence of ash in commercial Silver Label gelatin did not interfere with the

TABLE I

The isoelectric points of de-ashed gelatins as located by the pH for maximum intensity of scattered light at room temperatures

EASTMAN A		EASTMAN B		EASTMAN C		OSSEIN III	
pH	Tyn. Eff	pH	Tyn. Eff.	pH	Tyn. Eff.	pH	Tyn. Eff.
*4.65	1.6	4.92	13.4	4.88	4.1	4.37	1.9
4.87	2.6	*4.96*	14.3	4.90	9.3	4.42	2.2
4.90	11.1	5.02	10.6	*5.00*	11.5	4.76	5.3
4.95	12.9	*5.16	5.3	*5.03	5.9	*4.88*	5.8
5.03	10.6			5.13	0.9	4.95	4.8
5.10	9.7					4.98	4.4
5.12	6.7					5.06	3.2
						5.26	2.7

EASTMAN A′		SILVER LABEL		OSSEIN I	
				*4.80	—
				4.90	0.5
4.92	13.8	4.90	2.0	5.00	2.9
4.97	18.8	4.97	10.6	5.30	10.6
5.00	8.3	*5.01*	14.3	*5.52*	13.9
		5.07	0.8	5.90	8.4
		5.48	0.2	7.25	0.3

* Indicate the pH of one percent gelatin sols without added acid or alkali. Italics indicate the pH of maximum intensity of scattered light, and therefore, presumably, the pH of the isoelectric point within the limits of experimental error.

EASTMAN A and B: technical hide gelatins de-ashed by Eastman Kodak Co. by washing and precipitation of the gelatin.

EASTMAN C: technical hide gelatin de-ashed by protracted electro-dialysis of a molten gel and precipitation.

EASTMAN A′: prepared by a further electrodialysis without membranes of a 10 percent gel of Eastman A at 5°C.

SILVER LABEL DE-ASHED: "Silver Label," a high-grade hide gelatin de-ashed by electrodialysis of a gel at 5°C. This and the preceding specimen were kindly prepared by Dr. Ralph Mason.

OSSEIN GELATINS: prepared by Mr. J. R. Fanselow from purified ossein furnished by Hammond Organic Products Co. The ossein had been prepared by acid extraction of selected bones. It was treated with 0.2% sodium hydroxide for 3 months, changing the alkali every 3 days, to remove chondroitin-sulfuric acid, and other tissue impurities (Method of Knaggs and Schryver: Biochem. J., 18, 1079 (1924)). From this ossein, well washed with distilled water, 3 gelatin specimens were prepared by heating at 60°, 70°, and 80°C. Ossein gelatin I was further washed in Loeb's way (Loeb: J. Gen. Physiol., 1, 45 (1918)).

determination of the isoelectric point by the tyndallimetric method, it was assumed that other commercial gelatins might be studied in the same way. The data for room temperatures are presented in Figs. 1, 2, and 3. Fig. 1 refers to a series of calfskin gelatins, kindly furnished by the U. S. Gelatin Co., which were said to represent successive extractions of the same raw stock. In spite of considerable differences in quality and gel strength, the maximum light-scattering capacity, and presumably the isoelectric point, was practically constant at pH 4.9 to 5.0 for the entire series. In all cases, the light-scattering

capacity fell precipitously on each side of the maximum. Since the curves are almost discontinuous at the maxima, their exact heights cannot be determined; the maximum possible intensities therefore cannot be compared. However, the curves of Fig. 1 suggest the absence of any very striking differences in the maximum intensity for the five gelatins.

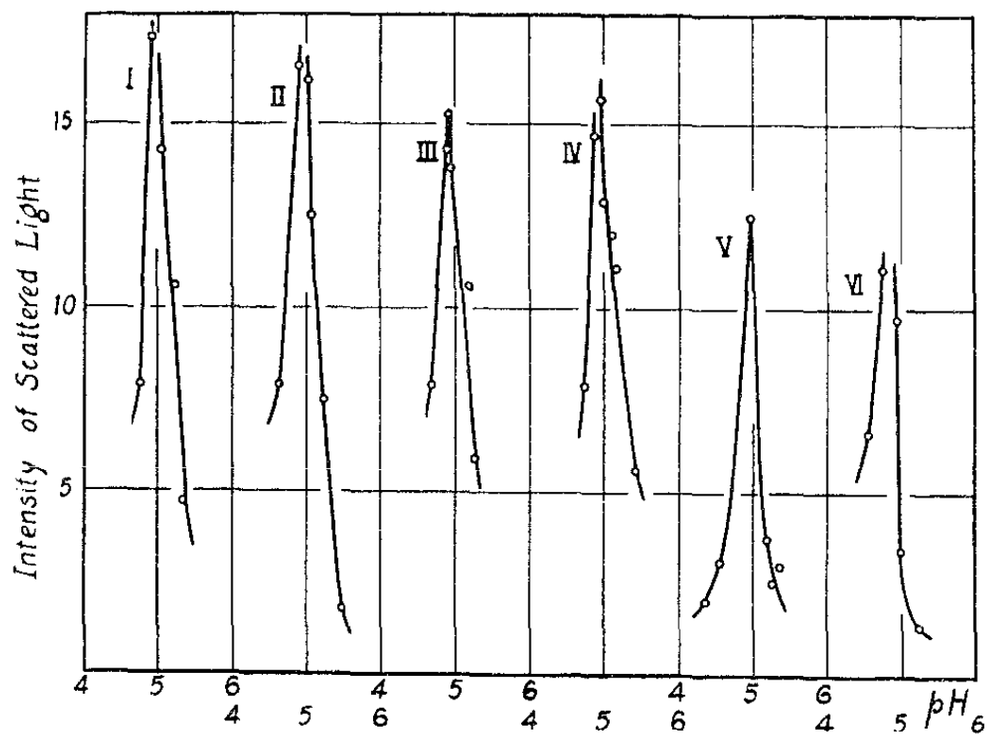


FIG. 1

Isoelectric points of successive extractions of calfskin gelatin stock as shown by the pH of maximum tyndall effect.

Fig. 2 presents observations on a series of Delft bone gelatins. Gelatins I-V were said to represent successive extractions of the purified bone stock, while gelatin VI was a special blended bone gelatin. Gelatin I, the highest grade member of the series, is seen to have resembled in its behaviour the "de-ashed ossein gelatin I" described earlier in this paper, for in both cases, the broad maximum fell near a pH 5.5. For succeeding members, the maximum intensity of scattered light shifted gradually toward pH 4.9 characteristic of the hide gelatins; at the same time, the height of the maxima fell decidedly. The ossein gelatins of Table I, it may be remembered, showed this same shift, a behaviour possibly characteristic of gelatin fractions from bone stock. These series of hide and bone gelatins might suggest that the two types could be distinguished by the character of these curves. This is shown to be erroneous by the striking resemblance between gelatin VI of the second group, described as a blended bone gelatin, and the hide gelatins of the first group with respect to the position of the maxima, although, it is true, the heights differ considerably.

The behaviour of other specimens is illustrated in Fig. 3 by data on three edible gelatins. "Cox" and "Knox" were blended gelatins of unknown com-

position and resemble the Delft blended bone gelatin. Of special interest is the pigskin gelatin with a maximum light-scattering capacity and isoelectric point (?) at the extreme pH of 8.

Gelatin Mixtures: In view of the probable heterogeneity of gelatins, it is of interest to examine the relationship between pH and light-scattering capacities of gelatin mixtures. One may wonder whether the components of a mixture would be revealed by the appearance of separate maxima in light-

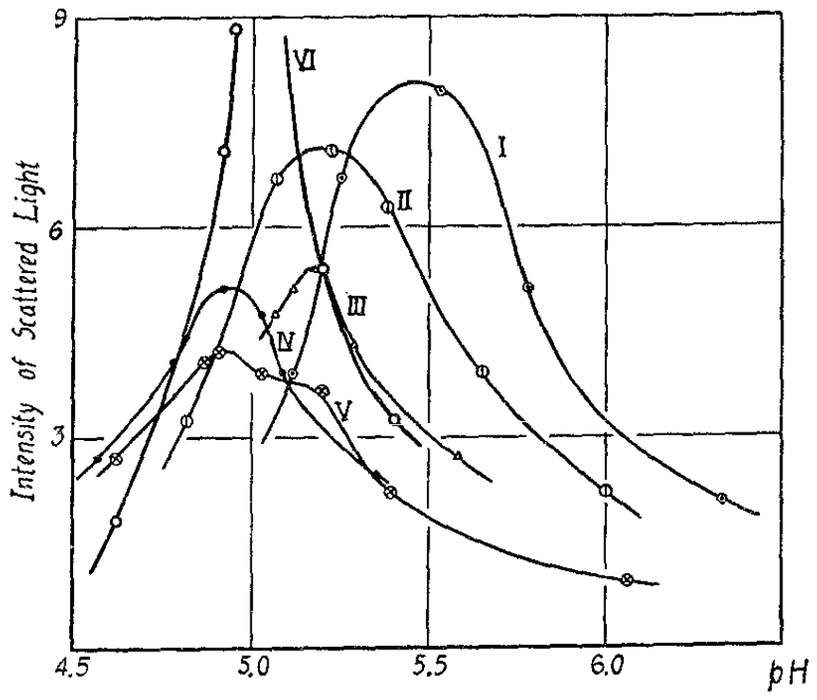


FIG. 2
Isoelectric points of bone gelatins
I-V Successive extractions of bone stock
VI Blended bone gelatin

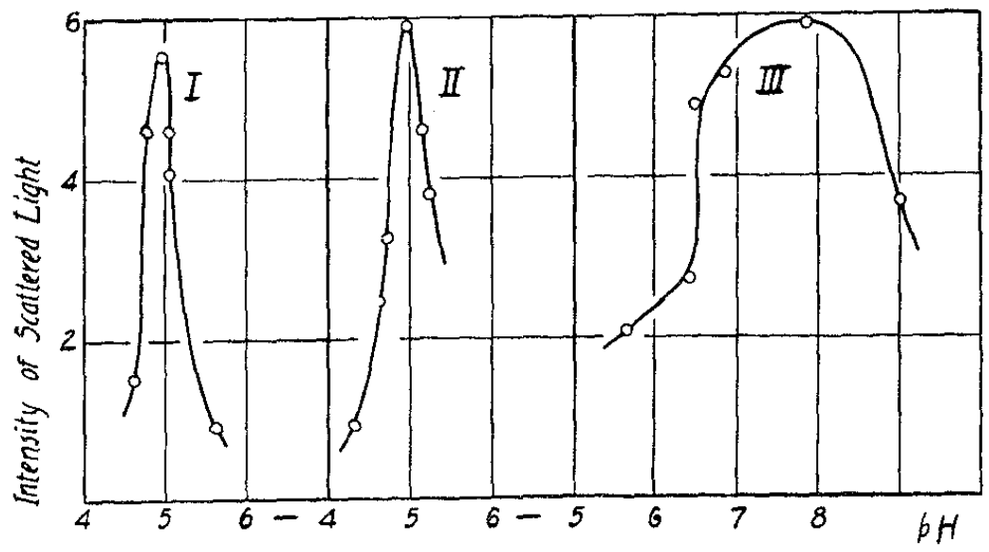


FIG. 3
Isoelectric points of various gelatins as shown by the pH of maximum tyndall effect.
I—Cox II—Knox III—Pigskin

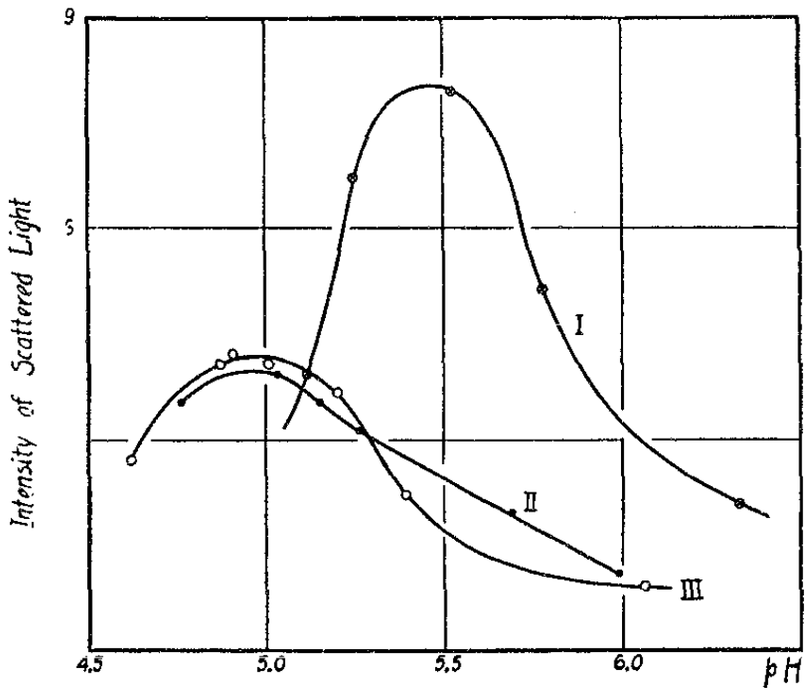


FIG. 4

Apparent isoelectric points of mixed bone gelatins.

I—Highest grade Delft bone gelatin. II—50% mixture of the highest and lowest grades of Delft bone gelatins.

III—Lowest grade of Delft bone gelatin.

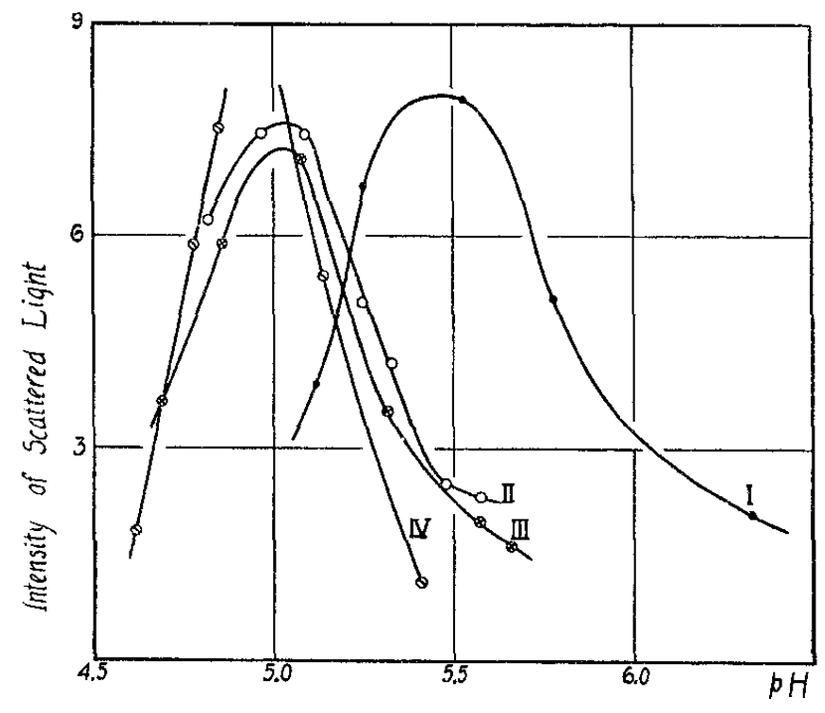


FIG. 5

Apparent isoelectric points of mixtures of calfskin and bone gelatins as shown by the pH of maximum tyndall intensity.

I—Highest grade Delft bone gelatin. II—90 percent bone gelatin. III—75 percent bone gelatin. IV—50 percent bone gelatin.

scattering capacity corresponding to the separate isoelectric points, or whether the precipitation tendencies of the components would be mutually modified to give a single new maximum tyndall effect or apparent isoelectric point. Figs. 4, 5, and 6 present observations at room temperatures on various mixtures of the gelatins discussed above. In no case were double maxima observed for a mixture; the components of the mixture were not revealed by the relationship between light-scattering capacity and pH. In Fig. 4, it is

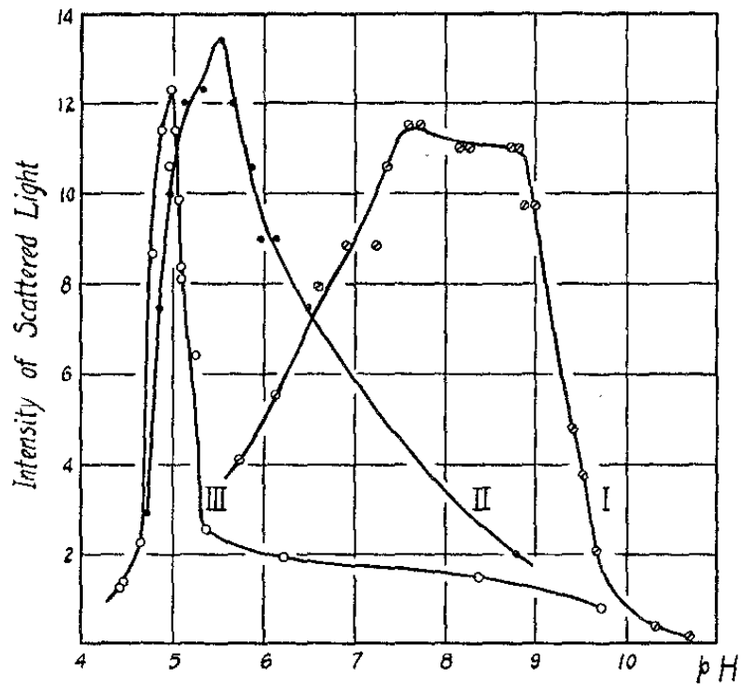


FIG. 6
Apparent isoelectric points of mixtures of calfskin and pigskin gelatins.
I—Pigskin gelatin. II—50 percent pigskin gelatin. III—10 percent pigskin gelatin.

seen that in a 50 percent mixture, the lowest grade Delft bone gelatin (V) practically effaced any evidence for the existence of an equal quantity of the highest grade Delft gelatin (I) in the mixture. This dominance of one component was even more strikingly shown in mixtures of calf-skin (I) and Delft bone gelatin (I) for which data appear in Fig. 5. Even 10 percent of the hide gelatin sufficed to give a maximum light-scattering capacity at a pH near 5. The intensity of the scattered light at pH 5.5, corresponding to the maximum for 90 percent of the mixture, was relatively low. Similar relationships are shown in Fig. 6 for mixtures of calf-skin (I) and pig-skin gelatins. In each case, the influence of the component with a maximum tyndall effect near pH 5 is more marked in determining the properties of a mixture.

Discussion: Following Chiari's original estimation (not based on any actual pH measurement) of pH 4.7 for minimum swelling, the older values assigned to the isoelectric point of gelatin usually fell near pH 4.6-4.7. The earlier work implicitly suggests the assumption that all gelatins are characterized by a constant specific value for the isoelectric point, Table II.

TABLE II

A survey of the determinations of the isoelectric points of gelatins

Author	Property showing maximum or minimum	A pH of dil. aq. soln.	B Nearest datum	C Range of uncertainty	D pH assigned by author	E Possible value
1. M G	cataphoresis			4.46–4.80	4.6	
2. P M	viscosity at 35°C. and alcohol no.		4.68	4.38–4.96	4.68	
3. L	a swelling and viscosity		4.9	4.2 –5.4	4.7	4.9
	b osmotic pressure		5.2	4.6 –5.5	4.7	
	c precipitation on standing	4.7			4.7	
4. JL	swelling	5.25	4.2	4.2 –7.0	4.6	
5. W V	turbidity				4.45	
6. R C	viscosity			wide	4.7	
7. B	a foam, viscosity, swelling			5.0 –5.2	4.7–5.0	5.1
	b gel strength, alc. no., turbidity			4.9 –5.4	,,	,,
8. S	viscosity			?	4.8	
9. W K	swelling		4.86	4.59–5.12	4.7	4.86
10. JL	turbidity	5.0+	5.0+	narrow	4.6	5.0+
11. M N	mutual precipitation		4.7	4.4 –5.0	4.7	
12. G B	a cataphoresis			4.73–5.08	4.9	
	turbidity		5.0	4.81–5.05	5.0	
	b ,,		4.98	4.96–5.20	5.0	
	c ,,		4.9	4.75–5.1	5.0	
	d cataphoresis			4.90–5.15	5.0	
	e ,,			5.30–5.82	5.55	
	f ,,			5.09–5.64	5.4	
	g ,,			5.42–5.60	5.55	
13. A D	precipitation on standing	4.87		narrow	4.7	4.87
14. H M	ultraviolet absorption			narrow	4.69	

TABLE II (continued)
A survey of the determinations of the isoelectric points of gelatins

Author	Property showing maximum or minimum	A pH of dil. aq. soln.	B Nearest datum	C Range of uncertainty	D pH assigned by author	E Possible value
15. H	a osmotic pressure	4.9	5.0	4.6 −5.5	4.7	4.9
	b viscosity	4.9	4.8	4.5 −5.2	4.7	
16. M	precipitation on standing	4.9+		4.90−4.95	4.9	
17. J	surface tension		4.8	4.7 −5.3	4.8	
18. C	a turbidity	4.8		narrow	4.8	
	b rate of crystallization	4.8		"	4.75	
19. M P	a turbidity with acetate buffer	5.1			5.00	
	b " " " hydrochloric acid	5.1			4.9−5.0	
20. S S	intersection of titration curves				5.6	
21. K D	tyndall effect		4.9	4.7 −5.0	4.9	
22. K F	a optical rotation			narrow	4.9	
	b resistance to shear			"	4.9	
23. B O	optical rotation			4.2 −4.9	4.7	
24. O K B	swelling			4.6 −5.1	4.7	4.8
	"			4.6 −5.1	5.2	4.8
25. G	turbidity	5.07	5.0	4.99−5.07	5.00	

Remarks to Table II

3a. Many other examples of same type.
3b. Irregularly subdivided pH axis confuses the location of the discontinuity.
5. pHs calculated
6. Very indistinct minimum
7. Semiquantitative curves. Several indistinct minima.
8. No data given
12a-d. Bone gelatin
12e-g. Hide gelatin
24. Equal within limits of experimental error.

References to Table II

1. Michaelis and Grineff: Biochem. Z., **41**, 373 (1912).
2. Pauli and Matula: Kolloid-Z., **12**, 222 (1913).
3. Loeb: J. Gen. Physiol., **1**, 363 (1918).
4. Jordan Lloyd: Biochem. J., **14**, 147 (1920).
5. Wintgen and Vogel: Kolloid-Z., **30**, 45 (1922).
6. Rawling and Clark: J. Chem. Soc., **121**, 2830 (1922).
7. Bogue: J. Am. Chem. Soc., **34**, 1343 (1922).
8. Sheppard, Sweet and Benedict: J. Am. Chem. Soc., **44**, 1857 (1822).
9. Wilson and Kern: J. Am. Chem. Soc., **44**, 2633 (1922); **45**, 3139 (1923).
10. Jordan Lloyd: Biochem. J., **16**, 530 (1922).
11. Michaelis and Nakashima: Biochem. Z., **143**, 484 (1923).
12. Gerngross and Bach: Biochem. Z., **143**, 533, 542 (1923).
13. Atkin and Douglas: J. Am. Leather Chem. Assoc., **19**, 528 (1924).
14. Higley and Mathews: J. Am. Chem. Soc., **46**, 852 (1924).
15. Hitchcock: J. Gen. Physiol., **6**, 457 (1924).
16. Manning: Biochem. J., **18**, 1085 (1924).
17. Johlin: J. Phys. Chem., **29**, 271 (1925).
18. Callow: Proc. Roy. Soc., **108A**, 307 (1925).
19. Modern and Pauli: Biochem. Z., **156**, 482 (1925).
20. Shukoff and Stschoukareff: J. Phys. Chem., **29**, 285 (1925).
21. Kraemer and Dexter: J. Phys. Chem., **29**, 1169 (1925).
22. Kraemer and Fanselow: J. Phys. Chem., **29**, 1169 (1925); Fourth Colloid Symposium, 110. (1926)
23. Bogue and O'Connell: J. Am. Chem. Soc., **47**, 1694 (1925).
24. Ostwald, Kuhn, and Böhme: Kolloidchem. Beihefte, **20**, 419 (1925).
25. Gerngross: Kolloid-Z., **40**, 279 (1926).

Since at that time the attention was naturally focussed upon the determination of the type of change in properties of gelatin systems near the isoelectric point, no particular effort was made to test the constancy of the quantity for different gelatins, or to locate with exactness the value for a given specimen. The tendency was rather to locate the approximate pH associated with a maximum or minimum in a physical property, and to assign to the isoelectric point the numerical value used by previous investigators. In any case, on account of insufficiently detailed experimentation,[1] inconsistencies in pH determinations by various workers, and ill-defined maxima or minima obtainable with many properties[2], it was not possible to discriminate between values differing by less than several tenths of a pH unit (or 100 percent differences in H ion activity). This indefiniteness is made evident upon comparing columns C, D, and E. The range of uncertainty in column C is expressed in terms of actual experimental observations between which it is dangerous to interpolate, particularly unless it has been shown by detailed experimentation that multiple maxima or minima do not occur.[3] In spite of these uncertainties, the differences between such experimental observations as are given in references 3c and 10—both by methods capable of locating the isoelectric point

[1] Illustrated by the range of uncertainty in references 3a, 3b, 4, 7b, 9, 14, and 23, of Table II.

[2] Illustrated in references 1, 2, 6, 11, and 23 of Table II.

[3] Sudden changes from minima to maxima very near the isoelectric point are shown by the rate of ice crystallization (ref. 16, Fig. 4), relative resistance to shear, gel formation and optical rotation (ref. 21b). The confusion which may arise as a consequence is illustrated by Fig. 7 of reference 16 in which the minimum rate of ice crystallization at pH 4.4 does not locate the isoelectric point. It is probable that the apparent discrepancies in isoelectric points as located by gelation and by turbidity in reference 12 were the result of these sudden changes in behaviour near the isoelectric point. Contrary to the usual assumption (see ref. 11), it was shown in ref. 21b that the maximum gel formation and maximum turbidity do not coincide in dilute gelatin systems.

quite sharply—would appear to exceed the probable inconsistency in pH measurement and therefore to suggest an inconstancy in isoelectric point. These differences were not generally noted, and it remained for Gerngross and Bach to demonstrate, in an insufficiently recognized paper, that the isoelectric points of gelatins may vary by as much as a whole pH unit. They found, as summarized in the table, the isoelectric points of four de-ashed *bone* gelatins to fall at pH 5.0 ± 0.1. On the other hand, three specially prepared and de-ashed *hide* gelatins possessed isoelectric points between pH 5.4 and 5.6. Eight commercial gelatins of unspecified source gave values between pH 4.45 and 5.05. Our data confirm the inconstancy in the isoelectric points of gelatins, suggesting even that it may extend to pH 8. There is however a curious and rather puzzling discrepancy. Whereas Gerngross and Bach found high values with hide gelatins, our high values were observed with bone gelatins.

Perhaps it should not seem surprising that the isoelectric points of gelatin vary. The inconstancy in chemical constitution has of course long been recognized. With the possible exception of some who have been particularly zealous in evaluating molecular weights, dissociation constants, and the like, students of gelatin systems have in general recognized the present impossibility of isolating and defining a unique chemical species in gelatin. This has been made clear by the careful work of Schryver[1] and his students, although much remains to be done in the fractionation and chemical characterization of the products of collagen or ossein "hydrolysis." The customary suggestion is that the lack of uniformity in properties of various gelatins may be due to the presence of a whole series of hydrolysis products between the original collagen and amino acids. And yet this suggestion is not an entirely satisfactory explanation of fluctuations in isoelectric point, for as Gerngross and Bach and others have shown, a given extraction or fraction of gelatin may be subjected to considerable hydrolysis without displacing the isoelectric point. In the presentation of the data of this paper, various of the hide gelatins were recognized as being of different grades, perhaps containing different quantities of hydrolysis products; but these differences were not accompanied by differences in isoelectric points. The available data give the impression that the isoelectric points fall into two groups, one near pH 5.5, the other near pH 4.9. Gelatin samples with maximum tyndall effects and isoelectric points between pH 5 and 5.5 may be mixtures of components corresponding to these two groups, which are not revealed individually, as illustrated by the data on mixtures in this paper. It is of interest and may be of significance that discontinuities appear to fall at the same pH's in the properties of gelatin precursors.[2] It thus seems possible that the fluctuations in the isoelectric points of gelatins may indicate inherent heterogeneities of some type in the gelatin precursors rather than be due to different degrees of hydrolysis.

[1] Schryver et al: Biochem. J., **15, 17, 18** (1921-1924).

[2] Porter: J. Soc. Leather Trades' Chem., **5**, 259 (1921); Thomas and Kelly: J. Am. Chem. Soc., **44**, 195 (1922); J. Ind. Eng. Chem., **15**, 1148; Wilson and Gallun: 71 (1923); Meunier, Chambard and Jamet: J. Intern. Leather Tr. Chem., **9**, 200 (1925). Discontinuities have also been found at pH 8 by Wilson and Daub: J. Ind. Eng. Chem., **13**, 1137 (1921).

As one possibility, the gelatin precursor may consist of two or more separate and distinct chemical entities which upon "hydrolysis" may yield gelatins with different properties and isoelectric points. Or, as another possibility, the gelatin precursor may possess structural (rather than simple chemical) heterogeneities of the type shown by Odén's sulfur and certain silver sols.[1] These systems are peculiar in that the quantity of "peptizing" agent required to give them stability in the sol condition varies with the degree of dispersion of the dispersed phase. The analogy suggests that different fractions of gelatin from given stock may be very nearly identical chemically and yet require varying acidities in the isoelectric condition. In either case, the isoelectric points of gelatins would depend upon the *characteristics of the precursors*. Elucidation of the cause for fluctuations in isoelectric point probably involves the problem of gelatin formation. At the present time, the choice between "hydrolysis" explanations and "peptization" explanations is largely a matter of personal preference. Both views are equally vague. Regardless of the mechanism of gelatin formation, the heterogeneity of many gelatins can scarcely be doubted.[2] As a consequence, the detailed interpretation of those aspects of gelatin behaviour to which it seems reasonable to apply the theory of ampholytes becomes a very difficult problem.

Influence of pH and Temperature upon the Light-Scattering Capacity of De-ashed Gelatin Systems

The sol-gel transformation of gelatin systems with change of temperature is an important and characteristic feature of their colloidal behaviour. Since it seems probable that gel formation is intimately associated with changes tending to precipitate formation[3], the relationship between sol-gel transformations and light-scattering capacities might be expected to be rather direct.

One aspect of these relationships is presented in Fig. 7, showing the dependence of light-scattering capacity upon H ion activity and temperature for gelatin systems containing, at 25°C, 1 g. vacuum dried gelatin (Eastman A, above) in 100 cc of solution. At temperatures of 40-50°C, where the gelatin was in a sol state, the light-scattering capacity was not great and was almost independent of temperature and pH. Only a relatively slight rise in intensity occurred in the neighborhood of pH 5. At these temperatures, a constant intensity of scattered light was attained practically as soon as thermal equilibrium. At lower temperatures, which bring about gel formation, there suddenly appeared an extremely pronounced maximum at a pH 4.95, the isoelectric point of the gelatin. In the range studied (pH 2.5-12.), this increase in tyndall effect was limited to the region between pH 4.5 and 7.5. Below pH 4.5 and above pH 7.5, a decrease in temperature from 50 to 17°C left the light-scattering capacity practically unchanged. The general form

[1] Odén: Nova Acta Upsala, **3**, No. 4, (1913); Z. physik. Chem., **78**, 682 (1912).

[2] Cf. also the case of casein, Linderström-Lang: Compt. rend. trav. lab. Carlsberg, **16** (1925).

[3] Cf. Kraemer: First Colloid Symposium, 62 (1923); J. Phys. Chem., **29**, 1523 (1925).

of the curve is asymmetrical. On the basic side of the isoelectric point, the influence of temperature appears somewhat more extended. The asymmetry is due in part to the use of pH notation (a logarithmic one), in part to the nature of the gelatin systems, for the same asymmetry in various degrees is shown by most other properties.

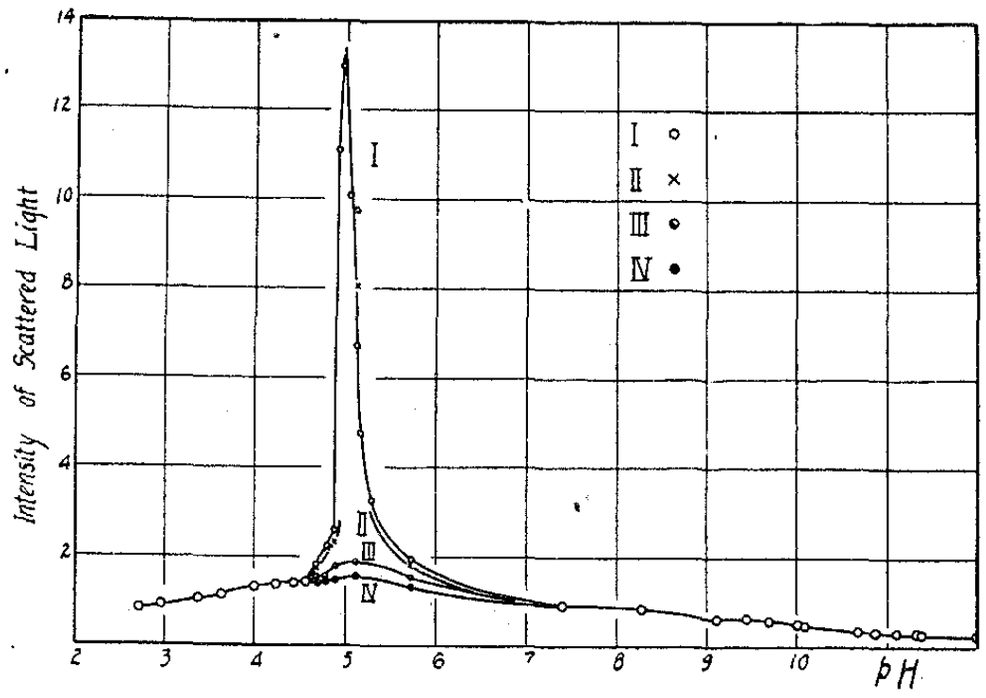


FIG. 7

Influence of pH and temperature upon the relative light scattering capacity of 1 percent de-ashed gelatin systems.

I—17°C. II—23°C. III—30°C. IV—40° and 50°C.

TABLE III

Influence of pH upon relative intensity of light scattered by one percent gelatin systems at 17°C.

pH	Intensity	pH	Intensity	pH	Intensity
2.71	0.79	4.90	11.1	9.46	0.71
2.96	0.89	4.95	12.9	9.71	0.66
3.38	1.04	5.03	10.6	10.01	0.57
3.63	1.10	5.10	9.74	10.09	0.53
3.98	1.32	5.12	6.70	10.71	0.37
4.23	1.37	5.15	4.78	10.88	0.34
4.35	1.42	5.28	3.25	11.12	0.30
4.42	1.37	5.73	1.96	11.35	0.27
4.56	1.41	7.38	0.94	11.40	0.24
4.65	1.62	8.19	0.94	12.00	0.21
4.66	1.84	8.30	0.89	12.10	0.21
4.79	2.21	9.12	0.71	12.22	0.19
4.87	2.59				

The abruptness with which the tyndall effect increases between 30° and 17°C is particularly striking. As may be seen in Table III, the relative intensity of scattered light increases about 430 percent for a change in pH but little greater than experimental error (4.87-4.90). Only 0.1 cc of 0.1 N hydrochloric acid was required to lower the intensity of 100 cc of a 1 percent isoelectric sol by 90 percent of the excess over the value, constant with temperature, at pH 4.65. After an increase in the height of the maximum by electrodialysis (Table I), the same quantity of acid gave rise to an even steeper drop. Since ca. 9 cc of acid were combined with 1 g. of gelatin at pH 1.7, usually considered as the point of complete combination, it is evident that only 1/90 or approximately one percent of the total combining capacity of the gelatin was involved in converting the gelatin from the "insoluble" isoelectric form to the sol condition. Four times this quantity of acid suffices to transform the gelatin to a form (at pH 4.65) in which the light-scattering capacity is practically independent of temperature. The dependence of tyndall intensity upon pH therefore does not parallel the combination curve for gelatin, but does resemble the rapid decrease in ease of precipitation with alcohol as the pH decreases from the isoelectric point.[1]

Discussion: In terms of the components of the systems, it appears that, in the sol state above 30°C, the solution units or gelatin micells are well defined and highly dispersed. Changes in equilibria, as a result of either pH or temperature change, take place rapidly and without hysteresis. Under all conditions of temperature or of combination with acid or base, the solution units possess a low absolute light-scattering capacity equal in order of magnitude to what one might expect in a dispersion of huge molecules. However, whether the solution units or micells above 30°C are uniform chemical molecules of gelatin or not is a question not to be answered dogmatically. To the extent that the light-scattering capacity above 30°C is constant with change of pH, it may be assumed as a first approximation that the size of the micells and their relative index of refraction, with respect to the solvent, is constant in order of magnitude. Since it seems improbable that decrease in temperature should greatly modify the relative index of refraction of the gelatin micells[2], the increase in light-scattering capacity at lower temperatures and near pH 5 may tentatively be supposed to indicate an increase in size of micells. In accordance with Rayleigh's formula, the relative intensity of scattered light for small particles at constant total concentration is proportional to the mean particle-volume. The tyndall effect curves therefore give an approximate picture of the variation in size (volume) of the gelatin micells.

Just at the isoelectric point, it is obvious from the superficial turbidity that the increase in size of micells has reached the advanced stage of gross

[1] Loeb: J. Gen. Physiol., **3**, 257 (1919); Pauli: "Colloid Chemistry of the Proteins", p. 46 (1922).

[2] The partial specific volume of gelatin shows no discontinuity, but changes gradually and normally with temperature. Cf. Taffel: J. Chem. Soc., **121**, 1971 (1922), and Davis and Oakes: J. Am. Chem. Soc., **44**, 464 (1922). It is therefore also probable that any chemical hydration which can be concretely conceived should not vary greatly with moderate temperature changes. Loosely bound water vaguely referred to as hydration, if any, might be expected to serve as part of the medium with respect to the scattering of light.

precipitation for which Rayleigh's formula is invalid. The discontinuity in light-scattering capacity is so sharp, however, that there is no necessity or advantage in attempting to apply the formula to the vertical portions of the curves. It is sufficient to point out that over a very narrow range of pH, the size of the gelatin micells shows a remarkable sensitivity to small quantities of acid or base. If dispersion of 1 gram of "insoluble" isoelectric gelatin into low light-scattering micells takes place by union of but one molecule hydrochloric acid per micell, the average equivalent aggregate weight at pH 4.87 (requiring 0.1 cc 0.1 N acid) must be 100,000.[1] As a compact cube of partial specific volume equal to 0.67,[2] such a micell would measure almost 5 microns on an edge—a very large unit to be held in the sol state by a single molecule of hydrochloric acid. Complete saturation of such a micell with acid (in the ordinary sense, i.e., 9 cc 0.1 N acid per gram of gelatin at pH 1.7-2.0) would require 90 equivalents of acid and involve evaluating 90 specific basic dissociation constants to characterize the micell as a base.

Without taking such estimations too seriously, one may yet readily recognize that the abruptness with which a trace of acid is able to convert the insoluble isoelectric gelatin into the sol state[3] is not to be coordinated with the simple theory of the solubility of ampholytes.[4] The mechanism of the process is shrouded in the general uncertainty surrounding the behaviour of gelatin at the isoelectric point. Harris, for example, suggests an extensive formation of zwitterions at the isoelectric point[5], and Modern and Pauli present evidence indicating that the hydrochloride formed with gelatin just adjacent to the isoelectric point is relatively slightly ionized.[6] This chemical complexity resembles that to be met in the stabilization by electrolytes of many well-defined disperse systems. Therefore, until greater clarity is attained, it seems preferable to apply tentatively the frankly noncommittal term "peptization" to both cases.

Besides the mechanism of sol formation by acid or base, the mechanism of the change at the isoelectric point as the temperature is raised, is but vaguely understood. From the curves of light-scattering capacity, it is clear that, as the temperature is raised, a significant change takes place in the temperature range 23°-30°C. Below these temperatures, a vanishingly small quantity of gelatin goes spontaneously into the sol state.[7] Above this temperature range, it is common experience that almost unlimited amounts of gelatin are dispersed spontaneously to give a sol of low light-scattering capac-

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[1] Cf. value of 96,000 found by C. R. Smith by osmotic pressure measurements of isoelectric gelatin at 30°C. J. Am. Chem. Soc., **43**, 1350 (1921).

[2] Wintgen: Kolloidchem. Beihefte, **7**, 260 (1915); Taffel: J. Chem. Soc., **121**, 1971 (1922).

[3] Also illustrated by data of Manning: Biochem. J., **18**, 1085 (1924).

[4] Michaelis: "Die Wasserstoffionenkonzentration" (1922); K. Sano: Biochem. Z, **168**, 14 (1926).

[5] Harris: Proc. Roy. Soc., **97B**, 364 (1925).

[6] Modern and Pauli: Biochem. Z., **156**, 482 (1925).

[7] According to Manning, about 10 grams in 10,000 grams of water. Biochem. J., 18, 1085 (1924).

ity, with some shift in the temperature range at high concentrations[1]. It is at present not possible to place definitely this phenomenon in the general classification of temperature displacement of equilibria. Some describe the case of gelatin in terms of the variation in true solubility of a homogeneous solid phase with temperature.[2] But a large temperature coefficient of solubility would be associated, according to van't Hoff's equation, with a large heat of solution of swollen gelatin. Such has never been observed.

On the other hand, it may be pertinent to analyze the peptization of isoelectric gelatin with increase of temperature and the critical solution phenomena from a common point of view.[3] In both cases, two phases of variable composition blend at a sufficiently high temperature to give one essentially homogeneous phase. Unfortunately for the gelatin case, the "critical solution temperature" is not sharply defined nor entirely independent of composition of the system. Such a situation could, however, conceivably arise if the gelatin contained a number of components of varying critical solution temperature which mutually interfered.

A third attempt at classification of gelatin behaviour might be made by comparing and aligning it with the equally striking behaviour of certain sulfur sols.[4] Although clearly heterogeneous, these sulfur sols in contact with coagulum behave very much like an ordinary saturated solution in contact with its solid crystalline phase. In gelatin sols and sulfur sols, an entirely reversible temperature equilibrium is displayed, as well as the abruptness of the temperature effect. In both cases, the abruptness increases with the extent of "purification." In the sulfur sols the ease of dispersion is greater for small particles, and appropriate methods of "purification" (i.e. fractional coagulation) yield a product with a relatively uniform size of particle and a surprisingly sharp critical peptization temperature. Superficially at least, the same observable effects follow the careful purification of gelatins. It is not at all impossible that the heterogeneity of gelatin systems may be not only chemical but also one of non-uniformity in size of particle (if this be the correct interpretation of the sulfur sol). Furthermore, it seems possible that a similar parallelism exists between sulfur sols and casein[5] or globulin[6] systems.

In spite of the attractiveness of the third case, it is scarcely possible to make a choice with certainty of success. The completion of the investigation of salt effects and light-scattering capacity now in progress will, it is hoped, furnish significant information relevant to this question. Although a recogni-

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[1] However, Jordan Lloyd claims that pure gelatin has a low "solubility" at even 100°C. J. Biol. Chem., **16**, 530 (1921). Inasmuch as Schryver's highly purified gelatin apparently did not show this behaviour, the point needs re-examination. Knaggs, Schryver and Manning: Biochem. J., **18**, 1079, 1085, 1095, 1102 (1924).

[2] Cf. Bradford: Chapter 47 in "Colloid Chemistry" edited by J. Alexander, (1926).

[3] Cf. Wo. Ostwald: "Die Welt der vernachlässigten Dimensionen", p. 74 (1922).

[4] Svedberg: "Colloid Chemistry", p. 228 (1924); Kolloid-Z., **4**, 49 (1909); Odén: "Der kolloide Schwefel", Upsala (1913); also Kolloid-Z., **8**, 186; **9**, 100 (1911), **10**, 119 (1912); Z. physik. Chem., **78**, 682 (1912).

[5] Linderström-Lang: Compt. rend. trav. lab. Carlsberg, **16** (1925).

[6] Sörensen: J. Am. Chem. Soc., **47**, 457 (1925).

tion of parallelism may give small comfort as an "explanation" of gelatin behaviour, the conversion thereby of many unique cases to a class with a common feature is a distinct step in the direction of a more detailed and presumably fundamental description of the phenomena.

Summary

Quantitative studies of the light-scattering capacity (tyndall effect) have been made in order to obtain in a direct way insight into the strictly colloidal behaviour of aqueous gelatin systems. The maximum tyndall effect located very exactly the pH defining the isoelectric point. By this method, it was shown that the gelatins may possess isoelectric points between pH 4.8 and 5.5 (perhaps even to pH 8.). Blended gelatins containing components with different isoelectric points behaved like a single gelatin with an intermediate isoelectric point. It was pointed out that part of the difficulty in quantitatively interpreting gelatin behaviour in terms of the theory of ampholytes is due to the fact that all gelatins may be mixtures of an unknown number of unisolated chemical substances.

A detailed study was made of the influence of acid, alkali, and temperature upon the tyndall effects of de-ashed gelatin. Above 30°C, the tyndall intensity indicated a high and approximately constant degree of dispersion at all pH's between 2.7 and 12.2. As the temperature fell below 30°C, an abrupt rise in tyndall intensity (i.e. a sharp fall in degree of dispersion) developed in the range of a few degrees over a fraction of a pH unit at the isoelectric point. A mere trace of acid or alkali sufficed to repress this change. A discussion was given of the significance of these facts for an understanding of the condition of gelatin in the sol state. It was suggested that the great effectiveness of acid or base in preventing the precipitation of de-ashed gelatin at ordinary temperatures is not to be interpreted in terms of the simple theory of ampholyte solubility. The analogies were discussed between the dispersion of isoelectric gelatin above 30°C and (1) solubility of a phase of constant composition, (2) conjugate solutions with a consolute temperature, and (3) colloidal systems with a critical peptization temperature. Gelatin and other protein systems may belong to case (2) or case (3), rather than to case (1).

NEW BOOKS

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. *By J. W. Mellor. Vol. VII. 25 × 17 cm; pp. x + 977. New York and London: Longmans, Green and Co., 1927. Price: $20.00.* And still the wonder grows that Mellor can turn out volume after volume in short order, since his only working time is in the evenings and the week-ends when he is not playing chess. The chapters in the seventh volume are entitled: titanium; zirconium; hafnium; thorium; germanium; tin; lead; inert gases.

"The pure element [titanium] has not been used to any great extent, but metal alloys have been used a good deal in ferrous and non-ferrous metallurgy. The ferro-titanium alloys are used as deoxidizers or denitrogenizers in iron and steel metallurgy, and they are also said to impart desirable qualities—*e.g.* toughness to the steel for certain purposes. According to Braune, the effect of nitrogen in steel is to increase slightly the toughness, and reduce the ductility. Hard steel with 0.030 to 0.035 per cent. of nitrogen is brittle, and soft steel with 0.05 to 0.06 per cent. loses its ductility. The presence of nitrogen is also said to favour the segregation of phosphorus and sulphur causing cold shortness. Titanium is said to remove the greater portion of the deleterious nitrogen from steel, at about 800°, by forming titanium nitride. For example, some remarkable results have been reported on the improvement of steel rails effected by the use of titanium. Thus the life of the rails in use is said to have been increased from 200 to 400 per cent. by the titanium treatment. Contradictory results have been reported on the effects produced by titanium in iron, because its action depends on the nature and proportions of the various constituents of the sample of iron investigated. Titanium alone does not readily alloy with iron and steel since it floats on the surface of the molten metal, and is difficult to dissolve; *master alloys* are therefore made—ferro-titanium, or ferro-carbotitanium—which when added to molten steel enable any desired proportion of titanium to be added to the metal. Silico-titanium or ferro-silico-titanium has been recommended when it is desirable to add both elements to steel. According to Rossi, the addition of one to two per cent. of titanium in molten copper by means of *cupro-titanium* as a master alloy eliminates oxide and absorbed gases and imparts a closer-grained structure than if titanium be absent, *mangano-titanium* is the master alloy which has been advertised as a deoxidizer in bronze manufacture. The effect of titanium on the magnetic properties of iron has been studied by Applegate—less than one per cent. of titanium in Swedish iron lessens the hysteresis losses; and increases the permeability whilst greater amounts increase the hysteresis losses.

"Titanium and some of its compounds have been employed in the manufacture of incandescent media for illumination—arc lamp electrodes, filaments for glow lamps, and gas mantles. The use of the metal or of the compounds of titanium—rutile, ilmenite, titanium oxide, or carbide, etc.—for this purpose depends on their high fusion and vaporization temperatures and their high radiation efficiency. Titanic oxide has been recommended in the manufacture of arc-lamp electrodes; and with rutile the results are said to be superior to those with carbon electrodes, particularly for street lighting. The positive electrode in the so-called *magnetite arc lamp* is made from a mixture of magnetite and chromite together with 15 to 25 per cent. of rutile or ilmenite, and it is operated on a direct, not alternating, current. It is claimed that this lamp gives a specially uniform distribution in a horizontal plane. It is also claimed that electrodes made wholly or partially of titanium carbide are comparatively free from the hissing of carbon electrodes, and that they give a steadier light and last longer. The use of titanium filaments for incandescent lamps has not been so successful on account of the rather greater efficiency of tungsten and tantalum filaments. Up to about two per cent. of titania in quartz-glass is said to improve the quality," p. 24.

"Titanous hydroxide is oxidized with the development of hydrogen: $2Ti(OH)_3 = 2TiO_2 + 2H_2O + H_2$, and at the same time the colour passes through various shades of brown, red, violet, and blue to white. Manchot and Richter found that when titanium sesquioxide is

shaken with an aqueous solution of potassium hydroxide and oxygen, a considerably larger volume of oxygen is absorbed than corresponds with one equivalent of oxygen. The hydrogen peroxide primarily formed is reduced partially by the titanium sesquioxide, the remainder of the peroxide oxidizing the titanium dioxide to pertitanic acid on acidification or possibly even in the alkaline solution. If a thick milk of lime or baryta-water is used in place of the potassium hydroxide, the hydrogen dioxide formed is not reduced by the titanium sesquioxide or dioxide, and the whole of the oxygen absorbed is found in the form of hydrogen dioxide. If the solution of tervalent titanium in sulphuric acid is boiled with potassium hydroxide, it evolves a volume of hydrogen equal to that of the oxygen absorbed on shaking the alkaline solution with oxygen. The acid solution also evolves hydrogen when boiled, but only extremely slowly. When shaken with oxygen, a solution of tervalent titanium in sulphuric acid containing ferrous ammonium sulphate absorbs a still larger excess of the gas, and the solution contains ferric oxide, whereas an acid solution of ferrous ammonium sulphate alone does not absorb a measurable volume of oxygen," p. 29.

"The facts favour the assumption that normal ilmenite is ferrous metatitanate, $FeTiO_3$, and that in the ferruginous varieties the metatitanate is isomorphously associated with ferric oxide; and that the ferrous metatitanate may also be associated in a somewhat similar manner with magnesium, calcium, and manganous metatitanates. Tammann found the temperature of formation from its constituent oxides is 700°. Ilmenite is fairly widely diffused in nature; it is a common constituent of igneous rocks, and appears to have been one of the earliest minerals to separate from the molten magma. It occurs associated with haematite in granites, syenites, diabases, gabbros, basalts, and other eruptive rocks. It also occurs associated with magnetite," p. 58.

"It is said that zirconium steel, i. e. steel with a small percentage of zirconium, is very hard and useful in making armour plates, armour-piercing projectiles, and bullet-shields. It is claimed that an armour plate one inch thick is equivalent to a plate of the best German steel three inches thick," p. 117.

"Mesothorium preparations are used in medicine as a substitute for radium preparations. Commercial mesothorium contains mesothorium-1, mesothorium-2, radiothorium, thorium-X, etc. Thorium minerals, monazite sand, or old gas mantles are used as raw material. This is digested with sulphuric acid. Part of the mesothorium is dissolved by the acid, but most remains undissolved. To prevent the dissolution of the mesothorium, a little barium carbonate or chloride is added. The liquid must be stirred so that the barium sulphate is formed throughout the whole mass of liquid; and enough barium salt should be added to precipitate all the mesothorium and radium in the solution. The mixture is treated with sodium carbonate to convert the sulphates to carbonates, or the sulphates are transformed into sulphides. The products are dissolved in hydrochloric acid, and the chlorides purified as in the case of radium salts," p. 187.

"Bunte and Luggin have shown that the trace of finely divided cerium oxide, on the surface of the thoria, is so active that under suitable conditions the mantle can be kept luminous in a stream of coal gas and air. A mica chimney is fixed over the mouth of a large Bunsen burner so as to form a prolongation of the tube. The mixture of gas and air is ignited at the mouth of the chimney, and the air supply is regulated so as to give a non-luminous flame. An ordinary Welsbach's mantle is then hooked by its loop on to a platinum wire, and is held on the burning mixture of gas and air at the mouth of the chimney, until it glows and emits light in the usual way. On lowering the mantle through the flame into the mica chimney below, it continues to incandesce in the cold current of air and gas," p. 216.

Wood, and Ives and co-workers give a hydraulic analogy for the behaviour of the burner and mantle. "Imagine the mantle to be represented by a vertical cylindrical tank into which water is flowing at a constant rate from a tap. Let the wall of the tank be perforated by holes of various sizes. The water which squirts out through these holes is the radiation, and the various sizes of holes represent various wave-lengths. If the smaller holes are more numerous at the top of the tank, then the higher the water rises the more will squirt out through the smaller holes, thus copying the behaviour of a material radiator, water

height being taken to represent *temperature*. If the tank contains many holes, the water will not rise very high, and, conversely, in one with only very few holes the water will rise higher, thus copying the behaviour of mantles of high and low emissive powers, in so far as their temperature characteristics are concerned. If the holes are all made small, only squirts of small size will be present, and the water will rise higher than if the holes of all sizes are present, thus copying the characteristics of a selective radiator like the mantle. In order for this tank to represent the behaviour of the mantle with respect to the amount of radiation, it is only necessary to imagine a vertical seam of the tank to have been left unsoldered, so that a bad leak is present, to represent the convection and conduction losses. The higher the water rises, as when the radiating holes are made in number, the more is lost through the leaky seam, and so the less is 'radiated' through the holes. Obviously, with a constant rate of supply the advantage of increased 'temperature is' being more and more offset by the leakage," p. 219.

The chapter on germanium, pp. 254-275 is to a very large extent an account of the work of Dennis and his students at Cornell.

The early Britons smelted tin ore by a very simple process. "They placed the ore in a hole in the ground, and laid wood between and around it. They then set fire to the wood. The fire smelted the ore. The slag was run from the molten metal through a pipe or furrow into a second hole. Many of these slag-hearths are still found in Cornwall. The whole smelting process was as effective as it was simple; proof of this is found in the fact that the slag residues do not contain sufficient ore to warrant a second separation by more modern methods," p. 276.

"Tin, though one of the common metals, is the most sparsely distributed metal in common use. The known workable deposits of gold cover one and a half million square miles, while the known workable deposits of tin cover but one-twelfth of this area. There is scarcely a country where gold has not been or might not be profitably obtained; tin is confined to about a dozen districts in the world. The tin deposits of Cornwall so long famed in history are nearing exhaustion; the same might be said of the deposits in Bohemia, Tuscany, South Spain, and the Pyrenees. There are, indeed, comparatively few known workable deposits of tin in the World," p. 280.

Somebody should study the colors of stannous oxide which may be black, bluish-black, slate grey, red, green, or greenish-brown, depending on the mode of preparation, p. 387. The author is distinctly non-committal on the subject of alpha and beta stannic acids, p. 405. On p. 426 is the extraordinary statement that a very dilute solution of stannous chloride raises the boiling-point of methyl acetate about twice as much as it should. Stannic oxide gives a reversible jelly with aqueous sulphuric acid, p. 479.

"J. N. von Fuchs studied the reduction of manganic salts by stannous chloride. A. V. Harcourt showed that the greater the amount of water employed in the solution of a given amount of stannous chloride, the greater the amount of a standard solution of potassium permanganate required for the titration. If air-free water be employed this phenomenon is not observed. The same amount of permanganate is required, however much water be employed. It was hence inferred that the oxygen dissolved in the water as well as the permanganate oxidizes the stanonus salt; but oxygen dissolved in water has no perceptible action on the stannous salt alone. Air can oxidize the stannous chloride only simultaneously with the permanganate. W. Ostwald called such reactions coupled reactions," p. 431.

"Lead emits a peculiar odor when rubbed between the fingers; the smell is probably not due to the metal, but to the organic substances—the fingers, for example, which come in contact with it. According to Percy, lead is feebly elastic or sonorous, and it furnishes a dull sound when struck with a hard substance; and the dullness of the sound, the 'leaden-ring,' is proportionate to the purity of the metal. R. A. F. de Réaumur reported that in 1726, Lemery discovered *par un pur hazard*, that if lead be cast into the shape of a segment of a sphere—*i. e.* mushroom-shaped—it has the novel and remarkable property of emitting sharp notes when struck with another piece of lead. The sonorous lead is rendered dull by hammering. Neumann also stated that lead cast into the form of a hollow spherical or

elliptical segment, is very sonorous. R. A. F. de Réaumur attributed the sonorous quality to the shape of the grains and to the way they touch one another. If the rounded grains are flattened by hammering, the elongated grains fill the interstitial spaces, and the particles are no longer free to vibrate, and the lead then emits a dull sound when struck. The velocity of sound in lead, according to Wertheim, is 1320 metres per second; and, according to Masson and Herz, in soft-lead at 15°-20°, 1227.4 metres per second," p. 524.

"Owing to the solvent action of the water supply on lead pipes in some towns in Lancashire and Yorkshire lead poisoning was prevalent for a considerable period before its real nature was recognized, and the cause discovered. Lead being a cumulative poison, may produce serious results if regularly taken in very minute quantities over long periods of time. The softest and purest water and peaty waters often act most readily on lead, so that lead has always been considered more or less dangerous metal in connection with the supply of portable water. These waters are treated with limestone to make them safe. The subject has therefore attracted a great deal of attention. The results of the various observations show that water of a moderate degree of temporary and permanent hardness, and containing but little dissolved nitrates and inappreciable quantities of ammonium salts, may be safely conveyed in lead pipes. Greenburg traced the lead in some cistern-water to the flashing on the roofs of buildings which collected the rain-water," p. 568.

"When plumbers strip the roofs of churches or other buildings, covered with lead which has lain undisturbed for many years, they usually find that side of the lead which is contiguous to the boards, covered with a white pellicle, as thick sometimes as a half-crown; this pellicle is corroded lead, and is as useful for painting, and other purposes, as the best white lead. The lead on the south side of any building is found to abound most with this white crust; that on the north side having very little, or none at all on it. It is believed, also, that lead which lies on deal boards is not so apt to be covered with this white incrustation, as that which lies upon oak: if there be any truth in this observation, it may, perhaps, be explained from hence, that oak contains a much stronger acid than deal, and this strong acid being distilled, as it were, by the heat of the sun in summer, attaches itself to the lead, and corrodes it: or this corrosion may be the effect of the sun and air, which, by their constant action, calcine or corrode the lead; and this calcined lead not being washed off by the rain, may, in the course of a great many years, form the crust here spoken of. Brame also observed the corrosion of lead in contact with oak, and Southerden said that the roofing of Axminster church laid on deal in 1833 was sound 85 years afterwards, but the portion laid on oak in 1909, was thickly encrusted with white lead after nine years. Dunsheath noted the corrosion of lead pipes in contact with oak. Cresse noted the perforation of sheet lead by a wood borer—Capricorn beetle, Goat beetle, or Sawyer worm," p. 573.

"Pliny also described how the Romans tested the harshness of wine by immersing in it a sheet of lead, and marking the corrosive action; they also sweetened some wine by boiling it in leaden vessels. Pliny does not seem to have thought the practice was attended by any danger. In the preparation of wine, if the fermentation process be carried too far, the liquor becomes charged with acid. The ancients probably knew that lead rendered harsh wine milder, and preserved it from acidity. The process was used with confidence because the toxic effects were not ascribed to the metal but to some other cause. The deleterious result of sweetening wine with lead compounds was mentioned by Citois in 1616, and Delamarc in 1696; and Zeller and Weismann said that the practice was invented in France. After the poisonous effects of this addition had been recognized, it required the severest of punishments—torture and death—before the use of litharge for this purpose could be stopped. Even in the eighteenth century, the improvement of wines by litharge was in some quarters taught as a method free from danger—*e. g.* by Graham—although J. Beckmann has cited a number of cases near the end of the seventeenth century, where those who treated the wines with lead compounds were very severely punished. The litharge or white-lead was singularly efficacious in renovating spoilt wine, but its effect on the consumer was disastrous. According to J. Beckmann, no adulteration of any article has ever been invented so pernicious to the health, and at the same time so much practised as that of wine

with preparations of lead; and as the inventor must have been acquainted with its destructive effects, he deserves, for making it known, severer execration than Berthold Schwartz, the supposed inventor of gunpowder.

"The wine occasions, according as it is used in a great or small quantity, and according to the constitution of the consumer, a speedy or a lingering death, violent colics, obstructions, and other maladies; so that one may justly doubt whether, at present, Mars, Venus or Saturn is most destructive to the human race," p. 588.

"Boltwood found the ratio of uranium to lead in primary minerals from the same locality to be so nearly constant as to suggest that lead may be the end-product of the degradation of uranium. The rate of radioactive change is so slow that direct proof of the degradation of uranium to lead cannot be expected. It has been calculated that a gram of uranium yields 1.25×10^{-10} grm. of radium-G per annum; and if the gram of uranium be constantly replenished to make up the loss, a gram. eq. of radium-G would require 8000 million years for its formation. A. Holmes has shown that with stable minerals of primary origin, where there is no geological or petrological evidence of the presence of lead as a primary product, and no evidence of the loss of any of the constituents by weathering, the age of the mineral can be estimated from the ratio Pb:U. The result shows that the age of some precambrian Norwegian minerals, in which this ratio is 0.103, approximates 1000 million years. The trustworthiness of the evidence was discussed by Kirsch," p. 602.

"Goebel found that the hardness of lead is increased by sodium from 4.1 when no sodium is present to 28.9 when 2 per cent is present; as the proportion of sodium is further increased to 5 per cent., the hardness drops to 18.4. Sperry, Thieme, and Mathewson also examined the hardness of these alloys. An alloy with 1.3 per cent. of sodium is called *noheet metal*, or *tempered lead*, and has been recommended as a bearing metal, and Patterson claimed that under these conditions some sodium hydroxide is formed, which, with the lubricating oil forms a kind of soap," p. 607.

"Henry found that when a bar of lead is bent in the form of a syphon, and placed with one end in the mercury, in due course the mercury will flow out at the other and lower end. With a bar made of non-hammered lead, the first drop of mercury appeared in 24 hrs., and when made of hammered lead, in 10 days," p. 618.

"Hatchett suggested that a systematic examination of all possible alloys of all the metals be made proceeding from the binary to the more complicated ternary and quartenary alloys. Supposing this were done, and that one proportion of each of thirty metals were taken, there would be 435 binary, 4060 ternary, and 27,405 quartenary alloys to be examined; and if four proportions of each of thirty metals were employed, 6655 binary, 247,660 ternary, and 1,013,985 quarternary alloys would have to be examined," p. 632.

"G. Kassner recommended the following process for preparing oxygen, with carbon as a by-product: porous calcium plumbate is moistened with steam and subjected to the action of washed furnace gases, preferably, at a temperature below 100°. The carbon dioxide of the furnace gases is rapidly absorbed, and the material, which retains its porous condition, then consists of a mixture of calcium carbonate and lead dioxide. This is transferred to a retort kept constantly at a red heat, and in this oxygen is evolved, the evolution being much helped by the introduction of a current steam. After the evolution of the oxygen, the current of steam is continued, and the temperature raised, when carbon dioxide is liberated, and may be collected for use. The calcium plumbate is then regenerated by means of a current of air."

Apparently iodine gives a blue color with lead hydroxide, p. 766, and bismuth sulphide changes the crystal form of galena from cubes to octahedra, p. 785. When galena is treated with acidified silver sulphate solution, a dark steel-blue film of silver is formed (colloidal silver or interference color?) p. 791.

"Carlson and Woelfel found that lead sulphide is not very soluble in gastric juice. Oliver said that no miner of galena has died of plumbism in England for many years, and Rambousek and Biondi added that plumbism is practically unknown among the miners of galena ore in Bohemia, but cases have been observed among the galena miners of Sardinia," p. 792.

Wilder D. Bancroft

Textbook of Biological Chemistry. *By James B. Sumner. 22 × 15 cm; pp. xxv + 283. New York: The Macmillan Company, 1927. Price: $3 50.* "The aim of the biological chemist is to explain the chemical composition of plants and animals and the chemical structure of the compounds present. In collaboration with the physiologist he must also explain such phenomena as the digestion and absorption of foods, respiration, the oxidation or catabolism of food materials, muscular contraction, glandular secretion, growth, regeneration, reproduction and the conduction of nerve impulses. While a vast amount of progress has already been made in the study of these problems by scientists of all nationalities, it must be admitted that only the surface has been laid bare. Much remains to be done. We are today unable to explain fully a single one of the processes listed above, indeed concerning the majority of these processes our present explanations are admitted to be entirely inadequate," p. 211.

"Metabolism is always in part catabolic and in part anabolic. The essential difference between the plant and the animal is that the reactions of the former are to a large degree anabolic, while the reactions of the latter are, for the most part, catabolic. The plant cell containing chlorophyll has the power to synthesize carbohydrate from carbon dioxide and water, under the influence of sunlight, and to synthesize amino acids, when supplied in addition with such simple raw material as certain inorganic salts. Power to carry on synthetic reactions of this sort is not possessed by the animal cell. The animal cell is incapable of storing the energy of sunlight and is, therefore, obliged to depend either directly, as in the case of herbivora, or indirectly, as in the case of carnivora, upon the plant for its supply of energy, as well as for its supply of the majority of the amino acids. The animal does possess synthetic ability in certain directions, however, and to a very considerable degree. For example, any one of the cells from the liver can build and repair itself; can synthesize fibrinogen, glycogen, bile pigments, and bile acids; can form urea from ammonium carbonate; can convert fructose and galactose into glucose; can convert glucose, or some degradation product of glucose, into fat; can detoxicate a great variety of poisonous substances; can form antitoxins; and can undoubtedly perform many other kinds of chemical work of a synthetic nature," p. x.

The chapters are entitled: the fats; the carbohydrates; acidosis; the proteins; vitamins; energy requirement; constituents of urine and their metabolism; the blood and respiration; physiological detoxications; enzymes; physical chemistry of protoplasm.

"Of the fatty acids only the members with an even number of carbon atoms are usually found in fats. Valeric acid with five carbon atoms is an exception being found in porpoise, dolphin, and whale blubber," p. 3. "The names given to the fatty acids are often taken from the origin of the fat containing them. Thus butyric acid is present in cow's butter, valeric in valerian root, caproic, caprylic, and capric acids in goat's butter, lauric in laurel oil, myristic in nutmeg (*myristica*) oil, palmitic is in palm oil, and stearic occurs in suet, the Greek for which is stear," p. 4.

"Liebig suggested that animals were capable of synthesizing fats from carbohydrates, but this view was abandoned when Voit and Pettenkofer brought forward experimental evidence to show that when dogs are fed on lean meat they store up a considerable amount of carbon, presumably as the carbon of fat. Other examples of a synthesis of fat from protein were supposed to be the formation of milk fat and the formation of fat in the so-called fatty degeneration of the liver and of nervous tissue. Some twenty years later Pflüger calculated the results of Voit and Pettenkofer and showed that these investigators had taken too high a value for the carbon present in lean meat and too low a value for the nitrogen, and that the recalculated results showed only a slight storage of fat in some cases and no storage at all in others."

"Physiologists now returned to the original view that fats can be synthesized by animals from carbohydrates. It was conclusively shown by Lawes and Gilbert, Soxhlet, Meissl and Strohmer, and several others that pigs, geese, and dogs, when fed on carbohydrate-rich food, are able to store considerable amounts of carbon in their bodies and that this carbon is in the form of fat. In these experiments the amount of carbon and nitrogen in-

gested were obtained by analysing and weighing the food and the excretion of carbon and nitrogen was estimated by collecting and analysing the urine, feces, and expired carbon dioxide.

"To-day it is accepted without question that animals synthesize fat from carbohydrate. It has been shown that ripening nuts contain carbohydrates. As the process of ripening proceeds, the carbohydrates disappear and fats take their place. When the nuts undergo germination, this process is reversed. This last reaction has not been shown to occur in the animal. The formation of some of the lower fatty acids from the sugars by certain bacteria is well known. Besides lactic and butyric acids, small amounts of caproic and caprylic acids have been observed to be produced. The manner in which the animal reduces carbohydrates to fats is not understood. It seems probable that some simple degradation product of glucose is used and that the fat is constructed by the addition of two carbon atoms at a time, since the fats that occur in nature nearly all contain an even number of carbon atoms. The synthesis of fat in animals does not take place unless the liver contains a large amount of glycogen.

"By experiments upon diabetic dogs, Lusk and others have shown that animals are able to synthesize sugar from protein. As sugar can be used by the animal for the synthesis of fat, it appears that fat might be produced indirectly from protein, with the intermediate formation of carbohydrate. It is unlikely, however, that a human being could consume enough meat to lead to a synthesis of fat, although a carnivorous animal might do so. Since the animal is capable of synthesizing fat from carbohydrate one might expect that fat need not be present in the diet, but the Germans suffered from a kind of edema during the war that was believed to be due to a lack of fat. This disease may have been due to the lack of the fat-soluble vitamins, rather than to the lack of fat itself," p. 25.

"In the normal animal, as has been pointed out, the oxidation of fat proceeds smoothly and completely and no more than minute traces of intermediate products can be isolated. On the contrary, when animals are suffering from severe diabetes, the oxidation of fat is incomplete and very large amounts of the products of this incomplete oxidation accumulate in the blood tissues, being found also in the urine. These substances are called the acetone bodies," p. 30.

"The acetone bodies appear when the animal is unable to oxidize carbohydrate (diabetes mellitus), or when the animal has very little carbohydrate to oxidize (starvation). During starvation the acetone bodies are produced in considerable amount, but in a normal person the quantity produced is not dangerous. It appears that the oxidation of sugar assists in some unknown manner the last stages of the oxidation of fats. In other words, it can be said that "fats burn in the flame of the carbohydrates." Aceto-acetic acid is believed to be one of the normal intermediate products of fat oxidation, but in the normal animal it is destroyed by oxidation as rapidly as it is formed," p. 31.

"Upon oxidation with bromine glucose is converted into gluconic acid, the aldehyde group being changed to a carboxyl. Boiling with dilute nitric acid oxidizes both ends of the glucose molecule with the formation of saccharic acid. By treatment with hydrogen peroxide the aldehyde group in glucose is not affected but the opposite end of the molecule is oxidized, giving rise to glycuronic acid. This substance is of especial importance to the biochemist as it is formed by the animal cell," p. 41.

"The polysaccharides are unreactive and of high molecular weight. They are insoluble in water, form colloidal solutions and for the most part will not diffuse through parchment or animal membranes. The constitutions of the polysaccharides are almost entirely unknown. Indeed this field is probably the most difficult one in organic chemistry. The most that we can say about the polysaccharides is that they are anhydrides of the sugars, and that upon hydrolysis by acids or enzymes, they are broken down first into intermediate products and finally into the monosaccharides," p. 55.

One would like to know why it is that "in rats the hexose sugars are absorbed from the intestine at a rate which is constant for each sugar and which is independent of the concentration of the sugar in the intestine," p. 58.

"That the diabetic animal is incapable of storing glycogen in the liver is shown by autopsies after death from diabetes. Some glycogen is found in the muscles, but none is present in the liver. However, this lack of glycogen in the liver is probably due to the fact that glycogen is broken down as fast as it is formed. The sugar-hungry cells are constantly calling for sugar.

"In a normal animal, when there is a plentiful supply of carbohydrate, some of this carbohydrate is transformed into fat. The formation of fat from carbohydrate either does not occur in diabetes, or else the fat that is formed is used up at such a rapid rate that none is deposited in the tissues," p. 65.

"While the proteins can be considered as anhydrides of the amino acids, they exhibit among themselves great differences in chemical and physical properties. These differences are doubtless due in part to the nature of the amino acids present and in part to the chemical structure. The insolubility of the keratins may depend upon the large amount of cystin present; the properties of gelatin may be connected with the high percentage of glycocoll. Fur and feathers (keratin) are of value on account of their indestructibility and their insulating air spaces. Ligaments (collagen) are remarkable for their strength, horns and claws (keratin) for their toughness. The protein in saliva (mucin) is an effective lubricant, while that in the arterial walls (elastin) is elastic and aids greatly in the circulation of the blood. The proteins in the crystalline lens of the eye serve to refract light. The fibrinogen of the blood is especially designed to stop leaks. The proteins of milk (casein and lactalbumin) have been prepared as food for the young mammal, those in egg yolk (ovovitellin) are to serve as food for the young bird.

"It seems probable that the cell uses protein, or the amino acids from protein, as material from which to construct hormones, enzymes, and antitoxins. Hereditary differences probably depend upon the immeasurably complex structure of the protein molecule," p. 112.

"The question of the proper amount of protein for the human diet has never been settled. Advocates of a low-protein diet believe that the use of large quantities of protein is not only economically wasteful, since proteins are more expensive than are carbohydrates or fats, but that it is even detrimental to health. Their chief argument is based upon the fact that the animal is unable to store protein above the small amount used for reconstruction and for growth, but is obliged to deaminize the surplus of amino acids and eliminate the nitrogen as urea nitrogen. Some advocates of the low protein diet believe that the production and elimination of urea in large quantities put a strain on the body. They also point out that diets high in protein are likely to give rise to intestinal putrefaction and that the specific dynamic action of protein, which is so much greater than that of either carbohydrate or fat, makes the consumption of large quantities of protein undesirable for persons living in a hot climate.

"Advocates of the high protein diet like to point out that the races of mankind that are accustomed to consume large amounts of protein are the most vigorous and the most successful, while the races that consume small quantities of protein are indolent and sluggish. Moreover, advocates of the high protein diet believe that a surplus of protein is necessary to assure resistance to disease.

"It has never been proved that a high protein diet is harmful, but it seems likely that a low protein diet is better suited to those living in the tropics on account of the heating effect of protein food. This is attested to by the fact that inhabitants of hot climates are nearly always found to prefer a low protein diet even when protein is readily to be obtained. Owing to the deficiency of certain proteins in amino acids, it is always possible that a diet that is especially low in protein may be close to the danger line, unless the food that is chosen contains protein of the highest biological value," p. 130.

"Plant foods are cheaper as a source of energy than animal foods and carbohydrates are cheaper than either proteins or fats. Feeding grain to live-stock is a very wasteful procedure. It has been estimated that if the grain that is fed to raise beef and pork in this country were used directly for human consumption instead, that a very large number of persons could be nourished with the food thus saved," p. 146.

"Urea was at one time thought to be formed in the body by the direct oxidation of the proteins. We now believe that the proteins are hydrolysed to amino acids before they are catabolized. Uric acid was at one time thought to be one of the precursors of urea, inasmuch as urea is formed by the oxidation of uric acid by certain reagents. It is now recognized that uric acid is formed by the metabolism of the purines and has no connection with the formation of urea. Creatin likewise has been thought to be a precursor of urea because of the fact that creatin is converted to urea and sarcosin upon heating with alkali. However, creatin does not give rise to urea in the animal body," p. 159.

"Creatin is called an extractive because it is easily extracted from the tissues by water. It is present in the tissues either in a state of adsorption, or loosely combined chemically. Creatin is present in meat soup, gravy, and beef tea and is partly responsible for the bitter taste of these substances," p. 161.

"The nucleoproteins are acid in nature and are responsible for the power possessed by the nuclei of cells to stain readily with basic dyes. As the chromosomes of the developing ovum are undoubtedly composed largely of nucleoprotein, the nucleoproteins can be considered to be partly, or wholly responsible for the transmission of hereditary traits and characteristics," p. 166.

"In birds and reptiles uric acid is produced in large amount, as it is formed not only, as in man, from the catabolism of the purines, but also from the proteins. According to A. P. Mathews, the reptiles originated in a desert and, together with their descendants the birds, are provided with the power of excreting their nitrogeneous waste in solid form in order to avoid losing water. Uric acid is capable of excretion in solid form on account of its insolubility.

"Minkowski performed a celebrated experiment by extirpating the livers of geese and showing that during the short period of time that the geese survived this operation they excreted chiefly ammonium lactate instead of uric acid. The small amount of uric acid excreted after the operation was thought to come from the purine metabolism, Minkowski's experiment proved that the liver of the bird is the site of a synthesis of uric acid. It has been found that perfusion of the surviving goose liver with ammonium lactate leads to a synthesis of uric acid. When ammonium salts of three carbon atom acids, or urea, are fed to normal geese, the production of uric acid is found to be increased.

"In man and the anthropoid apes, and also in the Dalmatian coach dog, uric acid is very largely the end product of the purine metabolism, while in other mammals it is merely one of the intermediate products. The similarity between the purine metabolism of man and the anthropoids (gibbon, orang-outang, chimpanzee, gorilla, etc.) is good evidence of the correctness of the theory of evolution. The case of the Dalmatian coachdog is anomalous," p. 175.

"Uncivilised tribes that live largely on meat seem not to desire salt in their diet. Stefansson states that he soon lost all desire for salt while living among the Eskimos and subsisting on their diet. On the other hand vegetarians show a craving for salt. This is true of herbivorous animals as well as of man. Herbivorous animals are known to travel long distances to salt licks, or to drink of salt water. The necessity for salt by herbivorous animals has been explained as due to the loss of sodium chloride due to the presence of potassium salts in the food. If the food contains large amounts of potassium salts the excretion of potassium will lead to a simultaneous loss of chlorine. It must be stated here, however, that this is as yet theoretical and has not been proved experimentally.

"During starvation the elimination of chlorides is very slight as the body conserves its supply. After a month or more on a salt-free diet death occurs. Chloride is necessary to the animal for the production of the hydrochloric acid of the gastric juice. Sodium ions are necessary for the life of all animal cells. For example the heart will not beat if the sodium ion is not present in the perfusion liquid," p. 190.

"A large number of substances have been found to have a specific accelerative, or activating action upon enzymes. The kinases, mentioned above, are distinctive in that they activate in an irreversible manner. The class of activators known as coenzymes affects enzymes in a reversible manner. In some instances the presence of a co-enzyme is essential

for enzyme action, in others the co-enzyme merely increases the activity of the enzyme. Co-enzymes are not destroyed by boiling, and are dialysable. Yeast zymase can be separated from its co-enzyme by filtration through a gelatin filter. The co-enzyme passes through, but the enzyme does not. The enzyme is not active in this case, but becomes so when the filtrate, or when some boiled yeast juice, is added to it," p. 228.

The author closes with a section on colloids chemistry—for which we are grateful. He does not make use of colloid chemistry in the rest of the book—which is unfortunate—and the colloid chemistry is rather primitive. One wonders what the student will learn from the statement, p. 259, that "particles of smoke are precipitated in the Cottrell process by highly electrified metallic plates." One difficulty is, perhaps, that the author adopts Loeb's point of view. "In certain instances a process has been claimed, by the school of colloid chemists, to be one of adsorption, when it is really a case of chemical combination. This is undoubtedly true in respect to the reaction between protein and acid, or alkali, as has been recently demonstrated by Loeb," p. 261.

Wilder D. Bancroft

General Chemistry *By Horace G. Deming. Second edition. 22 × 14 cm; xvi + 653. New York: John Wiley and Sons, 1925. Price: $3.50.* In the preface to the first edition the author said, p. viii: "It is hoped that this book may be appreciated for the things it has left unsaid. Most texts contain too much matter that properly belongs in a course in descriptive inorganic chemistry for students specializing in chemistry. By sacrificing such museum material as hypobromous acid, phosphoryl chloride, hydrazoic acid, and the usual long catalogue of variously colored inorganic salts, space has been gained for the development of such topics of lively interest as hydrogen ion concentration and its applications, an introduction to the chemistry of nutrition, electrochemical principles, and the constitution of matter. This last-named topic, too frequently left as a sort of afterthought, to be presented in a concluding chapter, has been interwoven with the text in such a way that the student examines oxidation and reduction, almost from the beginning, from the modern point of view."

In the preface to the second edition the author says, p. v: "In the second edition the opening chapters have been simplified and improvements have been made in the order of presentation. To accomplish this, Part I has been rewritten, having in mind the needs of those who have not had a preliminary course in chemistry. Many additional exercises have been added, to afford more freedom in the selection of problems suited to particular classes of students.

"Brief mention has been added of some of the striking recent developments in industrial organic chemistry, such as the direct synthesis of methanol and acetic acid, fermentation methods for the manufacture of glycerol and normal butyl alcohol, and the production of isopropyl alcohol and other non-hydrocarbons from petroleum. On the whole, however, the part devoted to organic chemistry has been somewhat curtailed, in order to gain space for a fuller discussion of the elementary principles of electrochemistry and a better exposition of the subject of precipitation. In this latter connection the researches of Brönsted and others have recently shown how futile are numerical calculations based on the supposed constancy of the solubility-product, in the case of most types of salts. Nevertheless, in a qualitative way, there are still some useful applications that may be made of it."

The subject is divided into a preliminary part comprising 188 pages; into a section on non-metals, 134 pages; and into a section covering the metals which contains 176 pages. There are many things in the book which the reviewer likes and some things with which he does not sympathize.

It seems a little inadequate to say, p. 23, that "still another temperature scale, called the absolute scale, is in common use in scientific work. In this there are 100° between the two principal fixed points, as in the Centigrade scale; but the freezing-point of water is called 273° and the boiling-point 373°." Is it desirable to put in the arrangement of atoms in sodium chloride and calcite as early as p. 34?

The number of molecules in a cubic centimeter of gas under standard conditions is 27×10^{18}, p. 35. "Otherwise expressed, there are as many molecules in a cubic centimeter of gas as grains of sand, each one-fiftieth of an inch in diameter, in a cubic mile of sand. But since the molecules of air are in motion, a better illustration of the number in this mere thimbleful of air would be a snowstorm. A fall of 27×10^{18} snowflakes would cover the whole United States, three million square miles, to a depth of about an inch."

The reviewer was glad to see that glue and gelatine do not form true solutions in water, p. 98; but it is not quite fair to compare the swelling of gelatine in water with the dissolving of sugar. The conclusions would have been quite different if tannin had been substituted for glue.

The reviewer is not certain whether it is wise to discuss osmosis, p. 104, in general chemistry, to explain an electric current flowing through a wire is "simply a stream of electrons, handed on from atom to atom, along the path of the current," p.141, or "to express oxidation and reduction in terms of electrons," p. 150. Chemical symbols are introduced on p. 44 and are explained on p. 177.

It is interesting, however, to read, p. 148, that "if you interview a professional chemist on any subject in which chemistry plays a part, you will soon discover that he has developed a sort of 'chemical instinct,' which enables him to tell just about what will happen when stated substances are brought together in new ways, or under new conditions. To a very marked degree, he has acquired the ability to reason chemically.

"Now it is precisely this sort of ability that the student must acquire, in some limited degree, if the present course is to yield him anything of permanent value. Long after the details of formulas and equations have faded from memory, he should be putting chemistry to some use, in his business, home, or avocation, For if the chemical mode of thought has once been mastered, any library will supply the necessary chemical facts," p. 148.

"It has long been known that the animal body contains small amounts of chemically combined iodine, which is chiefly localized in the thyroid gland, near the base of the neck. Experience has moreover shown that iodine, in very small amounts, is a necessary ingredient of the diet. Indeed, serious derangements of the health, of a kind now known to be due to a deficient supply of iodine, are common in certain communities in which the water supply and the soil (and consequently the crops produced locally) happen to be lacking in this element. Recently, in at least one such situation, arrangements have been made to add a definite small amount of sodium iodide to the water supply of an entire city, and 'iodized' table salt (containing a trace of sodium iodide) is now on the market," p. 236.

"We meet compounds of sulfur, particularly sulfuric acid and its salts, in almost everything we do. The water of our domestic supply is often clarified with aluminum sulfate or freed from algae with copper sulfate. Our soap is sometimes made from fat, with the aid of a catalytic agent prepared from sulfuric acid; or else with the aid of caustic soda, a substance often made by a process calling for sulfuric acid. The bristles of brushes are often softened with dilute sulfuric acid.

"The wool of our clothing is scoured with sulfuric acid, and bleached with sulfur dioxide, and the dyestuffs are fixed in the fiber with aluminum sulfate. The dyes themselves require sulfuric acid at several stages of their manufacture. The leather of our shoes is often prepared and tanned with the aid of arsenic sulfide and chromium sulfate. Shoe-blacking contains animal charcoal, purified with dilute sulfuric acid.

"At the table we meet glassware prepared from sodium sulfate. We may be served with cereal grown upon land fertilized with ammonium sulfate, gypsum (calcium sulfate), or superphosphate (made by the action of dilute sulfuric acid on phosphate rock). The very chinaware may carry a pattern of ultramarine blue, a sulfur compound. Sugar is often whitened by sulfur dioxide; and corn syrup is made by treating starch with dilute sulfuric acid, or an acid derived from it. Our newspapers contain wood pulp, which requires calcium bisulfite in its preparation, and often contains a trace of ultramarine. Printers' ink often calls for sulfuric acid in its manufacture.

"If we own an automobile we meet sulfuric acid in the storage battery, and various compounds of sulfur in the tires. Certain parts of the car were prepared for enameling by

pickling in dilute sulfuric acid. The nickel-plated fixtures were all plated in a bath containing nickel ammonium sulfate. Whether the upholstering is of real or artificial leather, sulfur compounds went into its preparation. The top is of fabric, impregnated with cellulose esters, prepared with the aid of sulfuric acid. Cellulose esters appear again in the celluloid windows and the body lacquer. The gasoline we burn comes from petroleum, purified by sulfuric acid. Our roadways are cut through rocky outcrops by blasting with dynamite, a substance requiring sulfuric acid in its manufacture. Even the Portland cement used in constructing concrete bridges, culverts, or roadbed always contains a small amount of calcium sulfate.

"We meet other sulfur compounds in our fountain pen, typewriter, telephone, varnish on our office furniture, writing paper, and the lithographed calendar on the wall. Even in our moments of relaxation we fail to escape from the compounds of sulfur, for cinematograph films, the insulation of wireless sets, piano keys, and a violin have met sulfuric acid, or substances prepared with the aid of sulfuric acid, at some stage of their manufacture. Indeed, our last act, when we retire at night, may be to turn a sulfur-rubber switch, thus breaking an electric circuit, consisting of copper wire, purified by electrolysis in a bath containing copper sulfate and sulfuric acid," p. 268.

The author gets the cart before the historical horse when he says, p. 275: "Aqueous solutions of acids, bases, and salts conduct the electric current. What more natural than to assume that this is because the charged particles *travel through the solution*, carrying their charges with them, and thus ferry the electricity across from one electrode to the other. For this reason they have been called ions (Greek, *going*)," p. 275.

The author says, p. 281, that "some recent work shows that many salts are very largely or perhaps completely dissociated even in concentration solutions;" but he does not give any further explanation. Some statement of the acids involved should be given if he is going to say, p. 296, that "strawberry juice tastes sourer than tomato juice because it has a greater momentary acidity; but titration with a base would show the tomato juice to have the greatest total acidity."

"The element nitrogen furnishes an excellent illustration of how men and women in the most diverse professions find common interests in chemistry. The biologist and the physician are interested in nitrogen because all the manifold phenomena of metabolism, growth, reproduction, and decay involve changes of this element from one state of combination to another. The architect and the civil engineer appreciate that land is cleared, building stones quarried, foundations excavated, and tunnels and canals built with the aid of high explosives—all nitrogen compounds. The farmer needs to take account of the ways in which the different forms of nitrogen in crops and soil are conserved, to win the greatest return from his acres, and reserve them for the future in undiminished fertility.

"The electrical engineer should know something about the processes by which nitrogen is brought into combination with other elements, to form ammonia and nitric acid, in electric furnaces; for some of the greatest developments of electrical power within the past few years have been in connection with these industries. Finally, the statesman should understand the relation of such nitrogen compounds as ammonia, nitric acid, and dyestuffs to the national defense; and should support legislation to encourage the production of fertilizers from the nitrogen of the atmosphere, to aid in supplying foodstuffs for the nation," p. 302.

"Tricalcium phosphate, or phosphate rock, $(Ca_3(PO_4)_2$, has already been mentioned as the principal phosphatic mineral. It is practically insoluble in pure water, and is accordingly but slowly absorbed by growing plants, when spread upon the soil as a fertilizer. Nevertheless, millions of tons of finely ground phosphate rock are used for this purpose, since it is gradually brought into solution by carbonic acid and other slightly active acids present in the soil. A plant with a vigorous and freely branching root-system, such as Indian corn, can make better use of such material than one lacking that advantage," p. 327.

"The most important higher alcohol is normal butyl alcohol, which is used in the preparation of normal butyl acetate, a valuable solvent. Normal butyl alcohol is manufactured on a large scale by a fermentation process. Corn mash, carefully sterilized by heat, is inoculated

with spores of Weizmann bacteria, which ferment starch directly to normal butyl alcohol and acetone. Air must be rigidly excluded, by carrying out the fermentation in deep vats or in the presence of hydrogen, and extreme precautions need to be taken to prevent foreign organisms from entering. To accomplish all this on a large scale has called for the development of methods that make this the world's outstanding example of Bacteriological Engineering—such interesting details as corn mash circulated through pipes previously sterilized by high-pressure steam; circulation pumps with pistons passing through loose packings wet with a solution of phenol (carbolic acid); and elaborate provisions for isolating a single spore of bacteria, and then propagating from this a pure culture sufficient to ferment the contents of a vat 20 feet in diameter and 20 feet deep," p. 359.

"The new lacquers used on automobile bodies (such as Duco finish) contain gums, pigments, and a variety of cellulose nitrate capable of forming a solution of low viscosity. The solvent is a mixture of esters, hydrocarbons, and alcohols. When exposed to the action of sunlight or ultraviolet light, the cellulose nitrate loses oxides of nitrogen, and reverts to a modified form of cellulose. The outer layer of the dried lacquer thus gradually becomes insoluble in the very solvents used in applying it," p. 366.

"Soap, in most cases, does not loosen and remove dirt by chemical action. This is evident from the fact that the substances removed may be of such utterly diverse sorts as clay, graphite, mineral oils, and saponifiable fats. If the substance to be removed is a film of oil, the rubbing breaks this up into minute droplets, which adsorb a film of soap and are thereby stabilized and prevented from reuniting.

"A second effect—and the more important one, in the case of solid substances like graphite—is an alteration of the surface condition of the textile fiber and incrusting substance, resulting in a weakening of the force of adhesion. Particles which previously clung firmly to the fabric are made to transfer themselves to the surface films surrounding the air bubbles that make up the foam of suds. This effect is mainly due to the trace of alkali (NaOH) which is always present in a soap solution as the result of hydrolysis, since the fatty acids, as a group, are *inactive*. It is only occasionally that the alkali acts chemically by entering into direct union with substances of acidic nature, such as rosin or free fatty acids," p. 366. The reviewer had supposed that no one now believes the washing action of soap to be due chiefly to free alkali.

Thousands of tons of corn starch are now converted each year into glucose sirup, used as a table sirup and in the preparation of confectionery. In spite of its name, the principal constituent of glucose sirup (commonly called commercial glucose or corn sirup) is not glucose at all, but dextrin, with smaller proprtions of maltose and glucose. The idea is to have enough dextrin gum in the sirup to prevent the sucrose or glucose from crystallizing out of the confectionery in which the sirup is used; and enough maltose and glucose to give the mixture considerable sweetness, and thus spare cane-sugar," p. 372.

"Many natural flavors and perfumes have already had to yield much of the field to their synthetic duplicates. Essences of lilac and lily of the valley are now made in ton lots, from turpentine; essence of violet from lemon oil; vanilla from oil of cloves; while blends in imitation of the elusive odors of the rose and heliotrope, together with fragrant mixtures never known in nature, are produced in large quantities," p. 381.

"An interesting speculation—though at present little more than a speculation—is that living organisms transfer food material from cell to cell by an arrangement of this kind. A cell wall may at one moment be permeable to water and water-soluble substances, but impermeable to lipoids (substances of a fatty nature). Then some substance appears which, like Ali Baba at the cave of the Forty Thieves, is possessed of the magic word. The wall structure is reversed, the lipoid passes through, and immediately the gates swing shut," p. 391.

"It is now very nearly a century since the first of the great host of organic substances known to the chemists of to-day was synthesized by artificial means, without the aid of living plants and animals. In the intervening years the science of organic chemistry has

developed at a rate which an age marked by tremendous scientific advances of all kinds could hardly parallel. The theory that the molecules of organic substances are composed of individual atoms, arranged according to definite and discoverable plans, proved a safe guide for hundreds of researches, which won the most brilliant results. As intellectual achievements, indeed, the most noteworthy mechanical inventions of the century just closed—such things as the automobile, airplane, and linotype machine—can hardly be compared with the synthesis of the complex molecules of indigo, camphor, and the medicinal alkaloids. The mechanic works with materials that he can measure and lay out with compass, square, and gauge; while the chemist must create his masterpiece from fragments too small for human senses, and can take note of the progress of his work only with the inner eye of the mind, as he adds atom to atom.

"These tremendous discoveries in the field of organic chemistry resulted not along in the creation of great industries rivaling or surpassing Nature in the creation of useful products, but afforded, year by year, a better understanding of the manner in which Nature herself works. A century ago all the processes involved in the digestion and assimilation of foods were complete mysteries, and the subject of the wildest speculations. To-day, we know, in a general way, what happens when foods are digested. The simplest of the chemical transformations that take place in nutrition are, indeed, so well understood that we can duplicate them in beakers and test-tubes. Progress is still very rapid in spite of many difficulties that surround experimental work with living animals and human beings. Biochemistry, in fact, is already very highly specialized. We can here offer no more than a glimpse of a few of the most important facts that have been discovered concerning the chemical changes that take place when foods are transformed into living tissue," p. 395.

"The electrical industries use an amber-colored variety of mica known as phlogopite, from Eastern Canada. In this a part of the aluminum of the transparent variety is replaced by magnesium and ferrous iron. It has nearly the same hardness as metallic copper, and is therefore useful as an insulator between commutator bars of dynamo electric machinery. Wireless telegraphy calls for large quantities in the manufacture of condensers," p. 414.

"Science is something more than accumulated information. Thus, at the conclusion of a course in General Chemistry, one should have gained something more than a collection of interesting or useful facts. More important than existing knowledge concerning the transformations of matter and energy are the *methods of thought* by which this information has been gained. One may have committed many chemical details to memory without having learned anything of chemistry, if one has failed to catch something of the spirit of the science, or to appreciate the attitude of mind in which a chemist approaches his problems.

"It is, indeed, as a product of human thought that chemistry is most impressive. The great peaks that dominate the chemical landscape—the laws that govern the infinite interactions of material things—were discovered for us by the creative efforts of individual men—the master-minds of the past. Thus the universe, from the scintillating sparks of the ultramicroscopic field to the mightiest of flaming suns, has been made to appear as the abode of order.

"No less impressive than the laws themselves, as intellectual achievements, are the general theories by which the laws find individual interpretation. Atoms and molecules, protons and electrons—what a world has been revealed beyond the limits of the mechanically aided human senses! Mere smallness hinders the scientist but little, when he sets out to count, weigh, measure, and analyze. Nor are all these triumphs of the past. Chemistry is a *growing* science; and those who labor for its advancement press forward in ever-increasing numbers, with confidence renewed by every new success. On the frontiers of all the principal fields of chemistry are important unsolved problems, and new ones are disclosed with each step in advance," p. 599.

Wilder D. Bancroft

Thermodynamics and Chemistry. *By F. H. MacDougall. Second edition. 22 × 14 cm; pp. vii + 414. New York: John Wiley and Sons, 1926. Price: $5.50.* The first edition was reviewed six years ago (**25**, 510), and what was said at that time in regard to the general character of the book still holds. The new portions include the work of Debye and Hückel on chemical equilibria in liquid solutions and a different treatment of the Third Law of Thermodynamics.

"In the first edition the method of treatment followed rather closely the historical development of the subject, a development which received its characteristic impress from the investigations and writings of Nernst and his fellow-workers. But although the great importance of the Nernst heat theorem is fully recognized, it is "now evident that the methods employed by Nernst in expounding and testing the heat theorem are unsatisfactory and roundabout and tend to obscure the essential simplicity of the Third Law. The author hopes that his treatment of the subject in the present edition will be found to be clear, direct, and adequate," p. iii.

The reviewer was interested in the treatment of activity, p. 271. "Since ideal gases and ideal solutions are never met with and since actual solutions and gases are frequently far from ideal, it has been found useful to introduce certain functions which tell us, among other things, how far the behavior of a certain substance or system departs from that characterized as ideal. A function called the *activity* has been proposed by G. N. Lewis. The activity, a, of any constituent of a solution or gas mixture, we shall define by either of the following equations:

$$\mu_1 = \Phi_1 + RT \log_e a_1,$$
$$d\mu_1 = RT\, d \log_e a_1 \text{ (T and p constant."} \qquad (10)$$

"Comparing equation (10) with equation (9), we observe that the activity of a constituent of an ideal gas mixture or of an ideal solution is *proportional* to its mole-fraction. It is evident that any function proportional to the activity can be put in place of a and still satisfy equation (10) and (11). Hence some additional specification is necessary before we can express the activity numerically. This specification may be made in different ways, depending on the nature of the problem. For example, in studying the activity of water in aqueous solutions, we may arbitrarily set the activity of pure water at the same temperature and pressure equal to unity. As regards other constituents of the solution we make use of the fundamental assumption that the behavior of a substance becomes *ideal* as its concentration approaches zero. Our addition specification may then take one of the following forms: the activity of a substance is set equal to (a) its mole-fraction, (b) its concentration, or (c) its partial pressure (for gaseous systems), as the concentration of the substance approaches zero. Corresponding to these three possibilities, the activity-coefficient γ_1 of any constituent is defined, according to circumstances, by one of the three equations:

$$\gamma_1 = \frac{a_1}{x_i};\ \gamma_1 = \frac{a_i}{c_i};\ \gamma_1 = \frac{a_1''}{p_i}. \qquad (12)$$

In this treatment Φ_1 is the value of the chemical potential of an ideal substance at unit concentration and is assumed to be constant. In fact Brönsted says that it is a constant by definition. This is the crux of the whole problem. One can of course make anything constant by definition; but that does not prove the definition to be a desirable one. If we have saturated solutions of sugar in water and in absolute alcohol, the chemical potentials of the sugar in the two solutions are the same because each solution is in equilibrium with solid sugar. If we do or do not ignore variations from the gas law, we can write $\mu_s = F_1 + RT \log p_1 = F_2 + RT \log p_2$, or $\mu_s = F_1 + f(p_1) = F_2 + f(p_2)$, where F_1 and F_2 are the values of the chemical potentials for unit concentrations. Since p_1 and p_2 are extremely different, F_1 and F_2 must also be different. The users of the activity concept have apparently assumed that F_1 is necessarily a constant for a solution because it is for a gas, although this whole matter was cleared up years ago by Lash Miller.

There is no definite statement, p. 278, as to the range of concentrations over which a strong electrolyte may be considered to be completely dissociated or as to what degree of strength is necessary before we postulate complete dissociation. Apparently nobody considers acetic acid as completely dissociated in tenth-normal solutions; but one would like to know whether the dividing line is drawn approximately at monochloracetic acid, dichloracetic acid, trichloracetic acid, or hydrochloric acid. Debye assumed, when lecturing at Cornell, that copper sulphate is completely dissociated because the color of the solution is independent of the concentration, and that cupric chloride is not because the color varies with the concentration; but there was at that time no independent way of checking these assumptions.

On p. 381 the author adopts the following statement of the third law of thermodynamics: "*The entropy of every pure crystalline solid is zero at absolute zero.* It should be noted that in any application to chemical reactions, there is no essential difference between the Nernst and the Planck formulation. We shall therefore make use of the latter on account of its greater simplicity and convenience."

Wilder D. Bancroft

Die Verwendung des Polarisationsmikroskops fur biologische Untersuchungen. *By August Kohler. No. 191, Abt. II, Teil 2, Heft 2. 26 × 18 cm; pp. 907-1108. Berlin: Urban and Schwarzenberg, 1926. Price: 9.30 marks.* This is an excellent book, but its title is a misnomer, the "*fur biologische Untersuchungen*" justifies its inclusion as part of Abderhalden's *Handbuch*, but appears to serve no other purpose. Any biologist who is looking for a simple key to a universal method will be disillusioned when he discovers that the emphasis is on the theory of the polarizing microscope and the general properties of anisotropic substances, and that specific applications to biology are hardly mentioned. He may seek this information in other works, but the reviewer doubts if he will ever find much that is worth while regarding the polarizing microscope in a few brief generalizations. If the biologist really wants to take advantage of an exceedingly promising method of studying his materials, he must resign himself to some intensive study of the principles employed. He must know the "why" and not simply the "how" of the optical tests he uses; otherwise the possibilities of misinterpretation are so numerous that fallacious results are bound to be frequent. On the other hand, if the polarizing microscope is used intelligently it may take the place of differential staining, dark field illumination, sectioning, or various other methods of preparation, so that living tissue may be studied much more completely than by ordinary means, in addition it is capable of yielding quantitative information of significance from the physiologists standpoint. Besides all this, the usual applications of polarized light to the identification of crystalline materials *in situ*, or as a product of micro-or macro-chemical reactions may supply information unobtainable by other means.

Köhler's manual constitutes an admirable course of instruction in the principles of polarization phenomena and the instruments used for their observation. Every page or so directions are given for a simple experimental demonstration of the intervening theory, and these 111 "*Versuche*" are much more illuminating than diagrams, though there are plenty of these also. If the reader actually carries out most of these illustrative practises he will have acquired a thorough working knowledge of the polarizing microscope, and he will have seen at first hand most of the type phenomena which he might utilize in obtaining information of the sort suggested above. It is to be hoped that his imagination and later his experience will enable him to try the proper tests on the proper specimen, and to draw appropriate conclusions from his observations, for here he will receive little guidance from the present work. In a handbook of methods, some space might well be devoted to results, particularly in new and undeveloped fields. As it stands, this book may fail to aid those who have most need of it, simply because of this lack of suggestive accounts of what can be done with the methods it discusses so clearly.

C. W. Mason

Practical Colloid Chemistry. *By Wolfgang Ostwald, with the collaboration of P. Wolski and A. Kuhn. Translated by I. N. Kugelmass and T. K. Cleveland. Fourth edition.* 20 × 13 *cm; pp. xvi + 191. London and New York: Methuen and Co.; E. P. Dutton and Company, 1926. Price: 7 shillings, 6 pence; $2.25.* Ostwald's "Kleines Praktikum der Kolloidchemie" is an excellent practical manual and an English translation of it was greatly to be desired. Unfortunately, the present translation is of little merit. Not only is it marred by ill-chosen phrases and ambiguous sentences, but in many places the sense of the original has been distorted almost beyond recognition and, in some cases, converted into nonsense. The omission of qualifying phrases results in some misleading statements, e.g. the 'Drop numbers' quoted on p. 35 might seem to be important physical constants instead of merely values obtained with a particular pipette; with regard to 'flotation' we find on p. 129 that "This process consists in freeing and purifying graphite from the earthy gangue by shaking with a suitable hydrocarbon"; while on p. 181 there is the startling statement, "Gold ruby-glass—This is almost colourless or faint yellow." The reader may be puzzled by the term "baryta filter" (p. 16) and will probably be still troubled when he finds (p. 28) that they are filters which "partially hold back freshly precipitated $BaSO_4$ and CaC_2O_4." The manner in which terms such as, "coalesce," "electrolysis" and "electrolytic" are used might also be criticised, but these are minor matters in comparison with the numerous real 'howlers' which can only be attributed to an incomplete understanding of the original text. On p. 53 it is stated that ". . . turbidity is greater in a solution of moderate concentration of the disperse phase"; the ultramicroscope is said to consist (p. 57) "of an intense Faraday-Tyndall cone which strikes a microscope with a special attachment to make colloid particles visible"; on p. 87 we find that, "Gelation includes the formation of a hydrated emulsoid, reversed by heating," while "swelling" turns out to be a very complex process, in that it "may be considered as a hydration, dissolution and a dispersion of hydrated colloid particles" (p. 105); Zsigmondy's "star dialyser" is, however, a simple contrivance—it "consists of durable parchment cups." Reference to the German text is certainly necessary in deciphering certain paragraphs. Thus, the sentence: "Such negative results are due to smaller particles in the emulsoid previous to hydration," (p. 59) should read: "Such negative results do necessarily indicate that the particles of the disperse phase are exceptionally small." ". . . the optical transition between disperse phase and dispersion medium was practically constant," (p. 61), and, "The kinetic methods involving a continuous change in one of the properties during coagulation have as yet not been sufficiently developed," (p. 135), are statements wrapped in obscurity. Finally, who would expect that the "native alumina" referred to on pp. 112 and 127 is really the well known "gewachsene Tonerde"?

The book is well printed on excellent paper in good binding and the only misprint noticed is on p. 8 where 'Ca' should read 'Cu'. Nevertheless, the student of colloid chemistry must exercise considerable discretion if he adopts it as a basis for his practical work: if he has even an elementary knowledge of the German language, the untranslated text is to be recommended.

H. J. T. Ellingham

Synthetic Rubber. *By S. P. Schotz. 26 × 19 cm; pp. 144. London: Ernest Benn, Ltd., 1926. Price: 21 shillings.* Although the synthesis of a substance identical with natural rubber has not been accomplished, many unsaturated hydrocarbons containing a conjugated double bond yield, on polymerisation, materials having many properties in common with natural caoutchouc.

Dr. S. P. Schotz devotes about a half of his treatise on "Synthetic Rubber" to an account of the preparation from various sources of Isoprene, Butadiene, and Dimethylbutadiene, which lend themselves to this process of polymerisation. Written from the practical point of view, well illustrated, and with ample references, brief but clear accounts are given of the various methods which have been employed for the preparation of these hydrocarbons.

The author then discusses the polymerisation of these substances, pointing out that it is the most difficult stage in the synthesis, and that the nature of the product may vary with

the method employed. This is followed by a short account of the Vulcanisation and Stabilisation of the synthetic product, and an outline of the properties and constitution of natural caoutchouc and the history of synthetic rubber.

This work is a useful summary of the present position of our technical knowledge of the subject, and the mass of information collected by the author should prove of value to those interested in this important question.

F. Francis.

Gmelins Handbuch der anorganischen Chemie. *Part XIII. Edited by R. J. Meyer Eighth edition. 26 × 18 cm; pp. xix + 142. Leipzig and Berlin: Verlag Chemie, 1926. Price: 22 marks.* This number deals with boron and the reviewer has found in it a number of things which interested him. "Boron is found both in plants and animals and is so wide-spread that one can distinguish only between organisms which are relatively rich or relatively poor in boron. Among the plants boron is found especially in grapevines. Boric acid tends to concentrate in the fruits. The grasses are very low in boric acid. Larger amounts are destructive to plants and prevent the formation of the chlorophyll dyes. When borax is added to fertilizers, wheat and oats take up very little boron, legumes and the succulent plants relatively large amounts. Wheat, beets, beans, and tomatoes contain boron chiefly in the tops of the plants, and, with the exception of beets, practically none in the roots. Tomatoes themselves contain only traces of boron while beans contain a good deal. Potato plants have relatively little boron in the tops and a good deal in the potatoes themselves. Boron occurs normally only to a small extent in animals, most being found in the marine organisms. Boron is one of the catalytically active elements of the living cell," p. 10.

All the earlier work on boron gave an impure product and Weintraub is apparently the first person ever to have produced what one might call pure boron.

The solubility of boric acid passes through a minimum in mixtures of water with methyl, ethyl, propyl, butyl, or amyl alcohol, and through a maximum with mixtures of water and acetone. The explanation offered, p. 81, for the occurrence of a minimum is that the alcohols bind water and thus decompose the boric acid hydrates. With increasing concentration of alcohol, boric acid alcoholates are formed which cause an increase in solubility. Since this explanation is undoubtedly wrong, it would be a good thing for somebody to study these systems carefully.

Wilder D. Bancroft

DETERGENT ACTION OF SOAPS

BY PAUL HENRY FALL

1404

I. Introduction

Soap is a product which has been used by the world from ancient times. Pliny, the great Roman historian, gives the earliest account of it as having been first made by the Gauls from a combination of goat's suet and the ashes of the beech tree. The word soap is used by the prophets Jeremiah and Malachi in their writings; but it is thought that possibly they referred to the ashes of plants and other such purifying agents.

In 1921 there were made in the United States close to 2.5 billion pounds of soap valued at approximately 250 millions of dollars.

Chevreul, a French chemist, raised soap making from empiricism to a scientific basis. It is altogether proper and fitting that this honor should be claimed by a Frenchman, as France for many years was the great soap market of the world.

II. A Survey of Factors proposed by Different Investigators as entering into Detergent Action of Soaps

Scientists have been far from unanimous in their explanations as to how and why soap cleans. Innumerable theories have been proposed by innumerable investigators.

Those reading this article who are not interested in this phase of the problem are advised to pass on to the next heading. But for the sake of a few, who may be unfamiliar with the variety and number of proposed answers to the question of why and how soap cleans, we will give the more important explanations which have been formulated by various scientists.

Berzelius[10] believed it to be due to the free alkali liberated by hydrolysis of the soap, Persoz[11], in 1846, shared this view with Berzelius.

Jevons,[12] in 1878, observed very pronounced "pedesis" (now known as Brownian movement) of particles suspended in a soap solution. He thought of the soap as loosening and washing away the dirt particles, which really amounts to a description but not an explanation of the problem.

Kolbe,[13] in 1880, thought the cleansing action to be due to the saponification of fats present by the hydrolysis alkali, and the entrapment of dirt particles by the foam, which permitted removal of the dirt by a mechanical process.

Wright,[14] assumed that the alkali formed by hydrolysis allowed contact of the water with the substance to be cleaned, that is, he thought the fact that a soap solution would "wet" oil while water alone would not was due to the alkali present in the soap solution. Hillyer[7] showed the wetting of the oil to be a property of the soap itself and not the of alkali of hydrolysis.

Ladenburg[16] quotes Knapp[15] as claiming the cleansing action of soap to be due to the property of soap itself of easily wetting oily substances, pene-

trating into the capillaries of the goods and acting as a lubricant, making the tissues and impurities less adhesive to one another and in that way promoting the removal of the dirt.

Chevreul,[5] Berzelius,[10] Persoz,[11] Knapp,[15] and others emphasize the emulsifying power of soap solutions and foams toward fats. Some believed this property to be due to the alkali of hydrolysis, others attributed it to undecomposed soap. No experimental evidence was obtained for either view.

Plateau[17] made extensive studies of substances which foam and of those which are emulsifying agents and laid the power of forming bubbles, films, and foams to two factors: high surface viscosity and low surface tension.

Quincke[18] shared similar views but ascribed the permanence of foam to the mixed character of the liquid, and claimed that no pure liquid would foam.

Hirsch,[21] in 1898, showed that fatty oils were not more readily emulsified than various other organic liquids, thus showing emulsification must be due to the soap itself and not to any alkali present.

Donnan[22] showed, in 1899, that emulsifying power and low surface tension (as determined by drop number) went hand in hand.

Kraft,[23] in 1895, insisted that soaps must be in solution in order to show any detergent action. He also believed the soap to be in colloidal, rather than true solution.

With only one or two exceptions all of the theories, up to 1903, of detergent action were founded on the belief that the alkali formed by hydrolysis of the soap was the active agent. At this time an excellent and luminous investigation was published by Hillyer.[7] He showed, as had Hirsch,[21] that the emulsifying powers of soap could not be attributed to alkali produced by hydrolysis. He further pointed out that alkali did not possess the property of wetting oily material as did soap. He demonstrated, as had Donnan,[22] the parallelism of low surface tension and emulsification and showed that saponin emulsified through the formation of a solid surface film instead of through low surface tension.

The extent of hydrolysis in soap solutions has been estimated as ranging all the way from neutrality to nearly complete hydrolysis. McBain and Martin,[26] and McBain and Bolam[27] state that the hydroxyl ion concentration is about N/1000 for most soap concentrations.

We are now at a point in the history of the theories of detergency where it is agreed that the cleansing action cannot be attributed to alkali.

In 1880 Hofmeister[28] considered soaps as materials of colloidal nature. But no attention was paid to this suggestion of Hofmeister's until in 1895 Krafft and Wiglow[23] pointed out that the more concentrated solutions of soap did not show the freezing-point lowering or the boiling-point elevation that would be expected of true solutions. They therefore stated that soap solutions were colloidal.

Further impetus to the development of this colloid notion of soaps, with added proof of the fact, was given by Goldschmidt[32] and Mayer, and Schaeffer

and Terroine[33] in 1908. After 1908 an innumerable number of investigators added weight to the colloid theory and it is now accepted as the main explanation of the detergent action of soaps.

According to McBain,[24] "the chemical formulae of soaps are well ascertained, tautomerism does not occur, true reversible reproducible equilibrium is established in all solutions, and finally the definite transition from typical simple electrolyte through colloidal electrolyte to neutral colloid may be observed in all stages. This transition from crystalloid to colloid is exhibited not only in passing from salts of the lower to those of the higher fatty acids, but may be demonstrated in any one of the higher members merely upon change of temperature and concentration. In alcohol, soaps exhibit a wholly different and much simpler behaviour. The soap here exists in the form of a simple unpolymerised electrolyte in true solution, whereas in most aqueous solutions it is of course a colloidal electrolyte."

Other factors in the detergent action, involving more or less, the colloidal properties of soap solutions have been emphasized by other investigators. Jackson[60] called attention to the influence which soap exerts upon the state of subdivision of the dirt. He observed Brownian movement when he examined, under the microscope, soiled fabrics immersed in soap solution.

In 1909 Spring[61] pointed out that all previous workers had been embued with the conception of dirt as being of a fatty or oily nature, or covered with a coating of such a material. He used lamp black which had been freed from all such material by washing with alcohol, ether, benzene, and benzene vapors. He found the detergent action of the soap quite unimpaired, and noticed that the suspensions would pass through filter paper without blackening it. He considered cleansing by soap to be due to the formation of a sorption compound, dirt and soap, in place of the sorption compound, dirt and fabric, by direct substitution.

Considering emulsions formed by soaps, Donnan and Potts,[64] in 1910, held that interfacial tension lowering was an important factor in stabilization.

Jackson[60] stated that lather was not necessary but was a sign of detergency. While it is true that lowering of surface tension does not always parallel foaming power (saponin produces foam but does not lower surface tension much) yet the alkali soaps lower surface tension markedly and produce foam in abundance. Stericker[71] claims that suds seem to lift the dirt out of the wash liquor thereby preventing redeposition, and that they act as a cushion in the power washer thus preventing injury to the materials being washed.

Linder and Zickermann[72] claim that wetting power is most closely related to lather tendency. Additions of saponin to the extent of 3% to all kinds of detergents tried in Berlin-Dahlem[73] failed to increase their value. Too great an emphasis has been laid upon the lathering power of soap.

From the discussion of the last several pages it is apparent that various investigators have added to or modified the views of their predecessors in this field, and that in some cases, quite contradictory views are held. But

following quite closely the outline given by McBain[24], a summary of a number of definite factors in detergent action, as brought out in the foregoing discussion, follows:—

(1) The necessity of having the soap in solution.

(2) It is essential in all cases that the soap should be in colloidal form.

(3) Power of emulsification which parallels low surface tension and formation of surface films, and depends, *not* upon the alkali of hydrolysis, but upon undecomposed soap.

(4) Wetting power which also depends upon undecomposed soap.

(5) Lubrication of textures and impurities which enable the latter to be removed easily. This might be considered as the action of the soap in forming non-adhesive colloidal sorption compounds with tissue and impurities due sometimes to acid soap, but more often to soap itself and capable of remaining in stable suspension.

(6) Deflocculation (peptization) of dirt particles. This is directly related to the preceding factors.

(7) Foaming power (to some extent).

As McBain states,[24] "comprehensive quantitative work is necessary to complete and coördinate the existing fragmentary work in any one case. Each of these factors is capable of simultaneous determination and quantitative evaluation."

III. Methods that have been used for measuring Detergent Action

Different investigators have worked on various phases of the detergent action of pure soaps, commercial soaps and soaps with known quantities of addition agents, much more work of a qualitative nature than quantitative having been done. The methods that have been employed have naturally been intimately connected with some of the factors that have been recounted. A list of the experimental methods hitherto published, as having more or less bearing upon the question, follows:—(Outline according to McBain[24])

(1) Measurement of surface tension against air by capillary tubes or by drop numbers or by bubbling or by measuring the amount of froth produced under definite conditions. (Rasser,[74] White and Marden,[75] Stericker[71] and others made use of such methods).

(2) Measurement of surface tension against oil or paraffin oil or benzene by drop numbers or measurment of emulsification. (Krafft,[76] Donnan,[22] Hillyer,[77] Elledge and Isherwood,[78] Briggs and Schmidt,[79] Bottazzi,[80] Shorter and Ellingworth,[81] Lenher and Buell,[82] Millard,[83] Richardson,[84] Stericker[71] and others have made use of one or both of these methods).

(3) Protective action as measured by gold numbers. (Work of this character has been carried out by Freundlich and Loeb[85] and Papaconstantinou[86] and others).

(4) Direct washing experiments with specially soiled clothes under controlled conditions of true temperature and concentration. (Such experiments have been carried out by Zhukov and Shestakov,[87] Stericker[71] and Heermann[89]).

(5) Measurement against carbon or other powders by measuring rate of sedimentation or protective action in filtration. (Qualitative work of this character was done by Spring,[61] while quantitative work was carried out by McBain and his co-workers[88]).

McBain and his co-workers[88] developed the first quantitative method for measuring detergent action. Up to the present McBain's method was the only one of a quantitative nature. But the procedure he devised is far from satisfactory either from a commercial or a scientific point of view.

McBain's Method and it's Limitations

McBain and his co-workers utilized the discovery of Spring[61] that soap solutions were capable of carrying carbon—only that portion stably suspended—through filter paper. The extent to which a soap was capable of doing this was considered a measure of it's detergent action. The carbon number of a soap solution represented the number of grams of carbon carried through by one kilogram of soap solution under standard conditions. The amount of carbon carried through the filter paper was determined by either gravimetric or colorimetric means[1].

Because of the limit of accuracy of an ordinary chemical balance the gravimetric means of determining the peptized carbon gives a possible error in the carbon number of about 10% for a 0.1 normal solution when only 10 grams of the filtrate are used. McBain used only 10 grams of the filtrate. If more than ten grams are taken the time consumed in filtering and washing is prohibitive. The probability of error from incomplete washing is very great when the amount of carbon on the analysis filter paper exceeds 10 milligrams. Since 10 grams of the filtrate were analyzed, this means that the method cannot be relied upon when the 10 c.c. of solution contain more than 10 milligrams of carbon.

Such a method, requiring so high a degree of accuracy and precision plus the great amount of time is obviously not applicable to universal use.

The colorimetric method is shorter. But when the colorimetric and gravimetric methods are compared the deviation is so great as to throw both methods in doubt.

TABLE I

Variation of Carbon Number with Concentration of Solutions of Neutral Potassium Myristate

Soap		Mean carbon numbers			
% Conc.	Normality	Gravimetric	Colorimetric	Difference	% Difference
1.32	0.05	0.17	0.21	0.04	23.5
1.96	0.075	0.47	0.32	0.16	31.9
2.59	0.10	0.49	0.41	0.08	16.3
3.22	0.125	0.54 ±0.01	0.54[2]	——	——
7.40	0.30	0.29	0.30	0.01	3.4

[1] For details of the procedure see reference 88.

[2] This indicates the standard upon which all colorimetric readings were based. Since this was determined gravimetrically there is no difference in the two methods in this particular case.

The results obtained by the gravimetric method were assumed to be correct in computing the present difference.

The fact that the percent difference is not constant is proof that the variation is not entirely a matter of difference in method of analysis.

If the gravimetric method is assumed correct, the colorimetric varies from it by 3.4 to 31.9 percent.

If the colorimetric method is assumed correct, the gravimetric varies from it by 3.3 to 46.8%.

These differences would certainly place the method outside the category of scientific accuracy.

In the colorimetric method it is necessary to weigh the filtrate from which the carbon number is determined. This is time-consuming and during the weighing some of the carbon tends to settle out. Thus a true aliquot part of the filtrate may not always be obtained.

Soap solutions have a definite color, and therefore as more concentrated solutions are used, a considerable error may be introduced in the reading of the colorimeter.

McBain's[83] method is based on a filtration process. He states, "In Spring's experiments with lamp black and in ours with carbon black only a portion of the carbon, that stably suspended, is carried through the filter paper. We utilize this fact and simply determine the amount of carbon black carried through".

We have found this method bad for two reasons.

First, there is a tendency for the carbon (or whatever form of dirt is being used) to be adsorbed by the filter paper. But also the adsorbed dirt tends to clog the openings in the filter paper, so that as filtration (with accompanying adsorption) is continued, it becomes increasingly difficult to filter the suspension and increasingly smaller amounts of carbon pass through the filter as the paper becomes more and more clogged. Finally the filtrate may be almost entirely clear (free from suspended dirt) if one continues to use the same filter paper. However, if a fresh, clean filter paper be substituted for the clogged filter, the suspended dirt will at first pass through quite easily but later with increasing difficulty and with less suspended dirt carried through as this new filter becomes clogged. (Undoubtedly this was much less noticed in the work by McBain and his co-workers since they filtered only about 10 cc. I was trying to filter 50 cc.).

That the above is really what takes place was proved by taking a good suspension of carbon in soap and by use of two or three different filter papers, finally getting a filtrate entirely free of unsuspended carbon. But the filtrate was very black due to a good suspension of carbon. Then this good suspension was poured onto a fresh filter paper. The first time it went through quite readily leaving only a very small amount of adsorbed carbon on the filter paper. Then this filtrate was again poured onto the same filter. This process of refiltering through the same filter paper was repeated several times. By the fifth or sixth time the suspension filtered very slowly, the paper became very black and the final filtrate was more translucent. In general it was ob-

served that the more concentrated the suspensions started with, the greater was the quantity of dirt adsorbed and the more rapid the clogging.

A second factor, causing a still more serious error, is the clogging due to suspended carbon (or whatever form of dirt is used). This error will be introduced in any method which causes unsuspended dirt to come in contact with the filter paper. McBain's method involves such contact for it calls for shaking the suspension one hour before filtering. In the interim, the carbon not truly suspended will, undoubtedly, not all settle to the bottom of the tube. Hence, in pouring the suspension on to the filter some of the carbon not in true suspension will accompany that that is in true suspension and the former will clog the filter very quickly and very appreciably so that in a short time most of the carbon that was in true suspension will be retained on the filter. This has been found to be the case in a large number of experiments which I have tried. (Since McBain and his co-workers filtered such small volumes the error introduced by the clogging of the filter paper would be small, but it would be no less real).

Since the accuracy of McBain's method depends upon the use of uniform papers (as well as accurate measurement of carbon suspended) it is apparent that if the openings are changed by the material being filtered, that comparable or concordant results cannot be obtained by this method unless the clogging of the paper is the same in all cases, which it is not.

McBain states,[88] "Some of the erratic results were undoubtedly due to faulty filter paper since occasionally some of the carbon coming through with the filtrate settled immediately to the bottom of the test tube and a second filtration through another filter paper reduced the carbon number to the expected value." He also states that a large number of filter papers were tested and No. 31 Whatman Filter Paper was finally adopted as being most porous and yet fairly uniform.

A further factor against this method is indicated by McBain when he states, "Table VI gives results for various concentrations of potassium oleate and here the filter paper was folded by gentle pressure between finger and thumb, since it had been found by Messrs. Allnutt that increased pressure may cause slower filtration and give inconsistent results."

It must be evident that, if a difference in pressure in folding the filter paper produces a noticeable or appreciable change in the amount of carbon carried through the paper, this method cannot be considered satisfactory for universal adoption.

While McBain's method appears to be the first quantitative method we have for measuring the detergent action of soap (hence a standard in terms of which the washing power of soaps can be expressed), yet it is evident, from the above discussion, that the method proposed by him is far from satisfactory. Therefore, before attempting to evaluate different soaps or to make a study of the factors which may be involved in the detergent process, an effort to develop an accurate, rapid and more practical method seemed not only justifiable but also necessary.

IV. Method of Attack

Dr. Bancroft suggested that if clay suspensions could be coagulated by the addition of small amounts of sodium chloride a quantitative means of measuring detergent action might be developed on this basis. The essence of such a method would be to form suspensions of clay with varying concentrations of soap solution and then determine the amount of sodium chloride which it would be necessary to add in order to cause flocculation of the clay. The suspension requiring the most sodium chloride would have the most clay in colloidal dispersion, and thus would possess the greatest detergent power.

If too much salt is necessary, this method would be useless as salt precipitates soap and this would vitiate the results unless a correction for this were made.

The conditions necessary for obtaining good suspensions of clay in soap solutions were first investigated. A 10% stock solution of olive oil soap was made (as received and not moisture-free); after this, however, all solutions were calculated on a moisture-free basis. By successive dilution the desired concentrations were obtained. 50 cc of solution were shaken thoroughly in 100 cc oil sample bottles with 1 gram of clay and allowed to stand. The solutions ranged from 10.0 to 0.0025%. The best suspensions were obtained at concentrations ranging from 0.625 to 0.156 percent. Above 0.625% the clay settled to the bottom in a compact mass. In concentrations below an 0.156% "flakiness and floating" occurred. That is, part of the clay floated on top and the remainder settled to the bottom in large flakes occupying two to three times the volume that it ordinarily would. The solutions in such bottles were perfectly clear and free from unsuspended material.

These concentrations were checked and rechecked and always the region of maximum suspension lay between 0.625 and 0.156% soap concentration.

Flakiness and floating was found to be a function of the dirt-soap ratio. Various amounts of clay were used ranging from 0.02 to 8.0 grams. When the amount of clay present was large in comparison to the amount of soap present, this phenomenon occurred. With 50 cc of a 0.1% soap it was observed with 2 grams or more of clay. With 50 cc of a 0.05% soap it occurred with 1 gram or more of clay.

Another point of note is that in no cases, not even when only 0.01 gram was used, was all of the clay taken into suspension. This points definitely to the fact that particle size must also play a big part in the formation of suspensions of clay, only those particles of an extremely small size being peptized.

Because of these facts, when considering a quantitative measure of detergent action it was necessary to use a definite amount of dirt in order for the results obtained to have any significance.

When using the salt method spoken of above the following results were secured.

A Absolutely no peptization of the clay was obtained when 50 cc of sodium chloride solution, varying in concentration from 10% to 0.00025% were shaken with 1 gram of clay.

B When increasing amounts of a certain strength of sodium chloride solution were added to a good suspension of clay in soap solutions, the amount of clay suspended appeared to decrease as the amount of sodium chloride increased. Finally, on further addition of sodium chloride, the clay became flaky and some of it floated to the top of the liquid. The liquid became practically free from suspended clay.

Table II will help to make this clear. 0.5 gram portions of clay were weighed out into large test tubes and the quantities of solutions added as shown in the Table. The contents were shaken vigorously, observed, allowed to stand over night at room temperature and again observed.

TABLE II

Effect of Sodium Chloride on: (1) Suspensions of Clay in Soap Solutions; (2) Soap Solutions alone

0.5 gram portions of clay (where used).
0.25% olive oil soap solution.
5.0% sodium chloride solution.
Room temperature.

Tube No.	Vol. of Sol. used Soap	NaCl	Results
		Clay present in the Following	
16	20	—	Good suspension for 30-40 hours
17	——	20	Clay settled to bottom in short time
18	19.5	0.5	Some clay still in susp. after 15-20 hrs.
19	19	1.0	About the same as No. 18
20	18	2.0	Very little clay in suspension
21	17	3.0	Practically no clay suspended
22	16	4.0	Solution clear. Clay flaky and floating
23	15	5.0	Liquid clear. Clay became flaky and floated to top almost immediately after shaking.
		No Clay present in the Following	
24	19	1.0	Solution slightly opalescent. No precip.
25	18	2.0	About the same as No. 24
26	17	3.0	Opalescence increased but no precip.
27	16	4.0	Opalescence still greater. No precip.
28	15	5.0	Milky but no precip. of soap until it had stood for a number of hours.
29	14	6.0	Precipitate of soap almost immediately.

It was found impossible to determine the amount of clay in suspension from measuring the amount of sodium chloride necessary to precipitate the soap. This is shown to be true by the fact that 50 cc of a suspension of clay in 0.25% soap required 4 to 5 cc of a 10% sodium chloride solution to flocculate the suspension and give flakiness and floating; with a 2.5% soap solution it

was necessary to add about 50 cc of the NaCl solution. But later experiments prove that a 0.25% solution will suspend more than twice as much dirt as will a 2.5% solution. It is noted that the amount of sodium chloride necessary to cause flocculation is in direct proportion to the amount of soap present. It is clearly seen that the amount of sodium chloride added gives a measure of the amount of soap present and tells nothing of any value as to the amount of clay in suspension.

C Experiments were also made in which equal volumes of soap of a given concentration were added to separate bottles containing clay and equal volumes of sodium chloride solutions of different concentrations. In each case the results practically paralleled those just reported. This was to have been expected.

The results thus obtained show that while sodium chloride can be added in sufficient quantity to flocculate the suspension before enough was added to precipitate the soap, nevertheless, the amount of salt required to flocculate the suspension is in reality a measure of the amount of soap present.

Ammonium chloride, sodium acetate, zinc chloride, cadmium chloride, and sodium nitrate were all tried in place of sodium chloride. They all gave results identical with those obtained with sodium chloride.

A gravimetric method was investigated with no success. This consisted of pipetting off a certain amount of the suspension and driving off the water at temperatures below boiling to avoid spattering. The evaporators containing the suspensions were then heated to constant weight. The gain in weight, minus the weight of soap present, gave the actual weight of clay suspended in a definite volume.

The results obtained were very erratic and of no value.

V. Development of a Practical Method for Quantitative Measurement of Detergent Action

Dirt is an all-inclusive term and may be applied to almost anything depending on the circumstances. However, it can be nicely classified into two physical states, namely, solid and liquid. We mean to confine ourselves in this investigation to the solid dirts.

As all attempts at gravimetric, colorimetric, and precipitation methods for determining solids in suspension have failed to be of any value it occurred to us that real progress might be made if we could use some dirt which could be determined quantitatively by a chemical means.

Manganese dioxide was considered. Experiments with clay, lamp black, ferric oxide, and manganese dioxide showed that all four of these dirts behaved very similarly in soap solutions. With olive oil soap and with sodium oleate they all showed maximum suspension in solutions of 0.625 to 0.156 percent soap solution. This proves manganese dioxide to be similar to other dirts that have been used by various investigators.

This substance is a very genuine dirt. Zsigmondy and Spear,[91] in discussing the work done on soaps by Spring[61] mention MnO_2 as an example of a substance free from fat which sticks to another surface. It is insoluble in

water and soap solutions and cannot be washed off by pure water; but is removed easily if soap is added. It can be analyzed for, quantitatively, by use of excess of ferrous ammonium sulphate, in the presence of sulphuric acid, and a subsequent titration with a standard solution of potassium permanganate. This is the method used in analyzing pyrolusite—the mineral MnO_2.

Experimental

Materials.

The materials used in the development of a quantitative method for measuring detergent action were the same as those used in the evaluation of different soaps (to be reported later) since the method and its application went hand in hand.

(a) *"Dirts"*. In an effort to obtain concordant results different kinds of MnO_2 were used. At the beginning of the work the stock-room supply of the oxide (commercial grade) was used. Later some C. P. MnO_2 from Scientific Materials Company was tried out. Then in the effort to get better results some of the stock-room supply was put through the Premier Colloid Mill using water as the suspending medium. After the dirt had settled to the bottom of the containing vessel, the supernatant water was decanted and the residue was washed five or six times by stirring and subsequent decantation of the wash water.

Then by means of specially constructed apparatus the washed suspension was levigated and thus the finest particles were obtained separate from the coarser.

Operation of Apparatus Shown in Fig. 1

At the start screw-clamp H is closed. The big jacket tube J (5 cm diam.) is first filled with distilled water flowing through tube D which is connected with bottle W by means of rubber tube C. Then screw-clamp H is opened to allow aqueous suspension of MnO_2 from bottle S to flow down the glass tube A (13 mm diam. and 120 cm long). Bulb B rests loosely against the end of the tube A and serves to "spread out" the suspension flowing down tube A. This "spread out" suspension is met by an upward current of distilled water (also "spread out" by bulb B) which tends to carry the finest particles up toward the top of jacket J and out through the overflow tube O.

The degree of separation of fine particles from the coarser depends upon the relative rates of flow of suspension from bottle S and of distilled water from bottle W. The rates of flow can easily be adjusted by means of the screw-clamps H and K.

The overflow (suspension of fine particles) empties into a large tall cylinder. The particles usually settle out on standing over night. Then the supernatant water can be siphoned off and the wet MnO_2 can be filtered by suction and dried.

Small equal volumes of the some of the levigated aqueous suspension were used in several determinations but this proved unsatisfactory because

of difficulty in controlling the amount of dirt taken for a determination. It also made difficult to control accurately the concentration of the detergent solution.

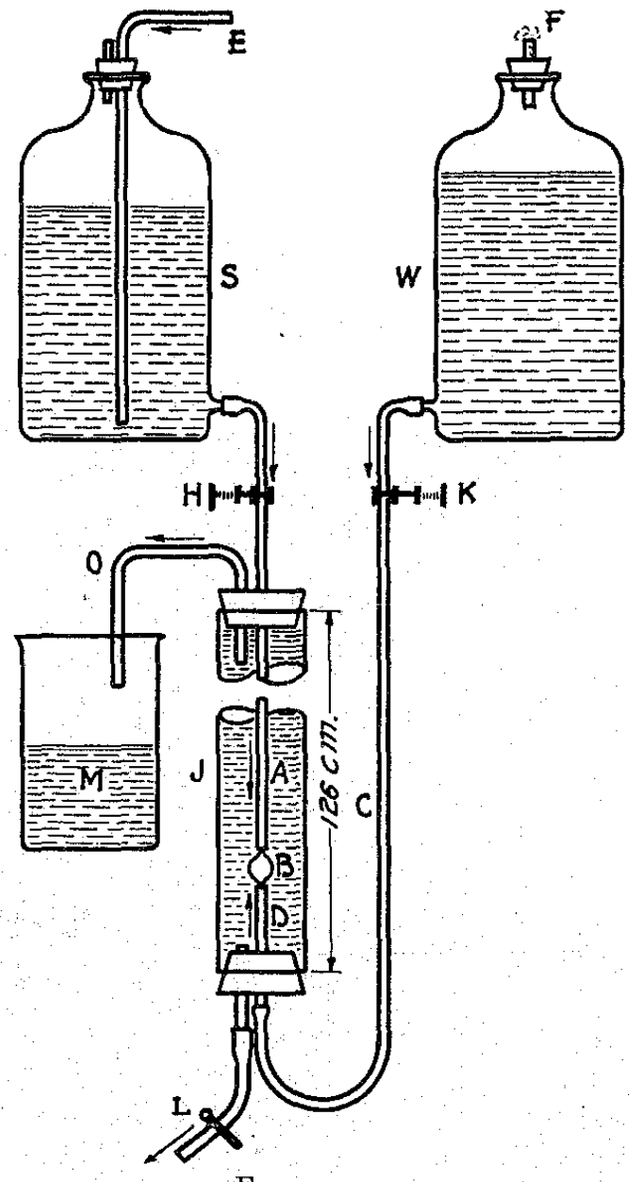


FIG. 1

E. Inlet for air to keep suspension stirred up
F. Loose cotton plug in glass tube.
S. Aquous suspension of MnO_2.
W. Distilled water.
H and K. Screw clamps to control rate of flow.
O. Overflow tube.
A and D. Inlet tubes (the arrow abreast of A represents flow inside the tube.)
B. Glass bulb to spread out liquids.
J. Jacket tube.
M. Cylinder for collecting fine particles.
C. Rubber tube.
L. Outlet for drawing off settled out mass of larger particles.

Finally some of this levigated aqueous suspension was filtered, dried in an oven at 60-70°C, ground in a mortar, put through a 160 mesh sieve, thoroughly mixed and bottled as a stock supply. This was designated as "Batch B-1, colloid mill MnO_2". This furnished more than 100 percent more suspendible particles than an equal weight of the untreated MnO_2.

Unfortunately, before all of the determinations given in this work were completed, this stock supply was exhausted. But another portion of the same levigated aqueous suspension was similarly filtered, dried, pulverized, sifted and mixed and a dirt giving very similar results to Batch B-1 was obtained. This was designated as "Batch B-2, colloid mill MnO_2".

Then still later, a shipment of Kahlbaum's "Precipitated MnO_2" was received from Germany and this was used in a number of different determinations.

(b) *Soaps.* Solutions of different soaps—olive oil soap, palm oil soap, tallow soap and sodium oleate of various concentrations were used. The analyses of the first three soaps named will be given later; the sodium oleate was a Powers Weightman product, labeled "Neutral." In most cases the dilute solutions were made by proper dilution of more concentrated or "stock" solutions. In other cases the solutions were made up directly from the solid soap. The "stock" soap solutions were kept in glass-stoppered bottles, the stoppers of which had been well vaselined, because of McBain's[88] indication that unless the stoppers were treated in this manner the CO_2 from the air entered and had a deleterious effect on the soap solutions.

(c) *Reagents.* C. P. ferrous ammonium sulfate from Scientific Materials Company and from Kahlbaum was used. Also N/10 solutions (standardized) of potassium permanganate, $KMnO_4$, made from C. P. crystals, obtained from the chemical store-room were used. These solutions were always allowed to stand in a dark cupboard 4-5 days after being made up, and were then filtered through asbestos before being standardized and used in subsequent titrations. When not in use, the solutions were kept in a dark cupboard. 6N solutions of sulfuric acid were made from the concentrated C. P. supply.

Procedure.

The method of procedure, to be described is of course a product of development, being quite different from the procedure as first attempted. In its present form it has been found very practical and yields quite satisfactory, though not ideal, results as will be explained.

(a) Making the suspensions. One gram portions of MnO_2, weighed within 0.2-0.3 percent, are placed in separate 100 cc oil sample bottles. Then 50 cc portions of the solution, of the kind and strength whose detergent value it is desired to determine, are added to each bottle. (It has been the custom to make triplicate determinations). Since most of the determinations are made at temperatures 15°-50°C higher than that of the room, the bottles—six at a time—of dirt and detergent solution are placed in a metal container (a gallon can provided with a tight-fitting cover) lined with heat-insulating packing and covered with asbestos. The container, with its contents, is laid in a motor-driven, horizontal, shaking machine and shaken the standard time—five minutes—at an average rate of 130 shakes per minute. At the end of this period of shaking the bottles are removed quickly and allowed to stand at room temperature, or, by means of spring clips which firmly grasp the necks of the bottles, the latter are freely suspended in a 40° or 75°C thermostat. Here they remain undisturbed for a period of four hours.

(b) *Separation of true suspension for analysis.* At the termination of the four-hour period, foam, if present, is dissipated by means of an electrically heated spiral of nichrome wire. Then by means of a special capillary siphon tube, 43 mm. depth of suspension, as measured from the surface, is sucked over into a large test tube connected to the delivery end of the bent siphon tube. By means of a threaded collar, which slips over the exposed portion of the siphon tube, the latter is adjustable to any desired vertical distance within a range of 2-3 cm. With this arrangement the intake (bottom of the capillary siphon tube) is always adjusted to be exactly 43 mm. from the surface of the suspension, the total average depth of which is 65-68 mm. Thus the intake of the siphon tube is 22-25 mm. from the bottom where the unsuspended dirt has settled. When suction is applied to the test tube, all of the suspension for a depth of 43 mm, as measured from the surface, is sucked over into the test tube.

Description of Fig. 2.

Tightly fitted into cork K is a female-threaded brass tube L. H is a slightly smaller brass tube with male threads to match threads in L. H is just large enough to permit the glass siphon tube (capillary) S to be moved up or down as desired. By means of the collar J which rests on the brass tube H, S can be adjusted and fixed at any height desired, since J has a set screw. The threads on H and L permit vertical adjustment of S for 2-3 cm. without resetting collar J.

Cork K fits tightly into chimney C, which is wide at the base and large enough throughout to slip over a 100 cc oil sample bottle B, which contains the suspension to be separated from unsuspended material at the bottom.

Burned into the siphon tube S at exactly 43 mm. from the bottom end (intake) is a small piece of glass, A, which acts as a permanent mark. Closely adhering to the outer walls of the siphon tube S and fastened to it, are fine, insulated copper wires, W W, which terminate in platinum points P_1 and P_2. The latter extends 3-4 mm. below mark A while the end of P_1 is exactly even with mark A. The wires W W pass through tiny holes in cork K and connect in series with a dry cell and galvanometer.

T is a large test tube which fits over the two-holed rubber stopper containing the delivery end of siphon tube S and the bent glass tube R. By means of rubber tubing the latter is connected with a Chapman suction pump through a small separatory funnel F, which acts as a safety trap.

Operation of Apparatus shown in Fig. 2.

Chimney C is slipped over the bottle B while siphon tube S and the closely adhering and fastened wires W W pass through the mouth of the bottle. (It is best to have H screwed up high enough so that mark A comes *above* the surface of the suspension, when the bottom of the chimney rests on the table top and collar J rests on H). After S is inserted H is turned down until P_1 just touches the surface of the liquid. This is determined by observing the galvanometer. Since soap solution conducts the electric current, the instant P_1 touches the surface the circuit is completed (since P_2 reached

the surface before P_1) and the galvanometer deflects. This gives a very sensitive and accurate means of determining when S is "set" so that the intake is exactly 43 mm. from the surface of the suspension. Furthermore, the chimney C becomes covered with "fog" when siphoning hot solutions and this makes it impossible to see whether mark A is exactly at the surface. Since the galvanometer is very sensitive, foam must be expelled for it con-

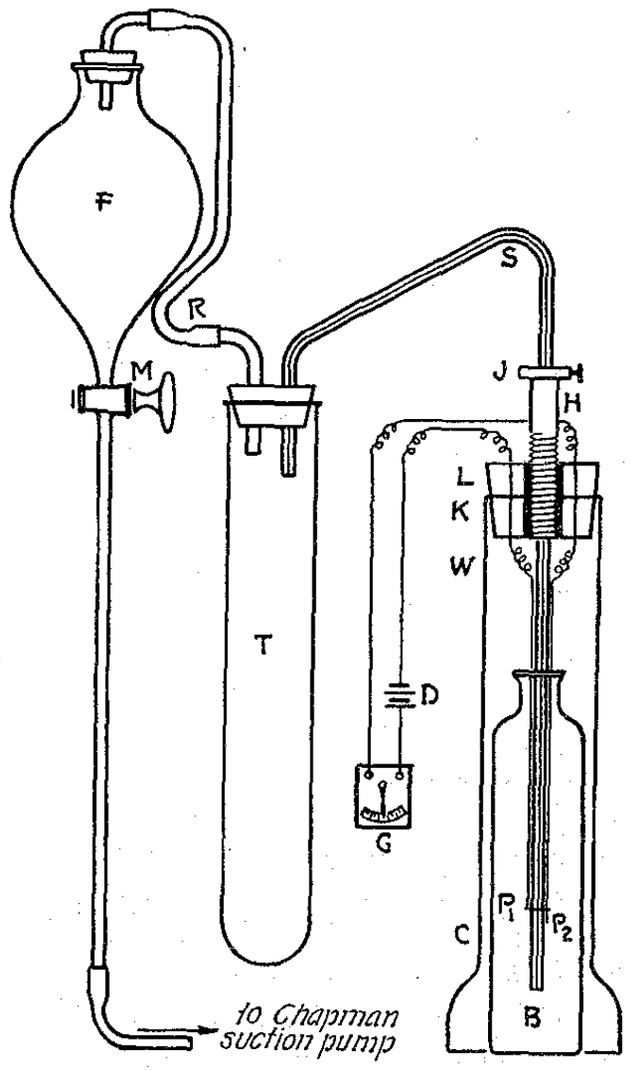


FIG. 2

Apparatus used for separating true suspension from unsuspended material.

ducts sufficiently to cause the galvanometer to deflect before the wire P_1 reaches the surface of the liquid.

When the siphon tube is "set", glass stop-cock M in the separatory funnel F is opened and suction left on until no more suspension comes over into the test tube T. This happens when the surface of the liquid in the bottle comes *below* the intake of the siphon tube. The stop-cock M is closed, tube T and bottle B are removed and others put in their places. The method is rapid—suspensions can be separated at the rate of one per minute. The volume of true suspension so obtained varies between 33-38 cc depending on the cross section of the bottle. And thus easily, quickly, and completely, true suspen-

sion to be analyzed is separated from dirt not in true suspension. The efficacy of this method for separating true suspension from unsuspended dirt will be discussed later.

(c) *Determination of the amount of MnO_2 present.* The suspension in the test tube is shaken to insure uniform distribution of suspended particles. Then, by means of a pipette, 25 cc of the homogeneous suspension are removed and added to a 500 cc. Erlenmeyer flask containing a known amount, but more than enough, ferrous ammonium sulfate (dissolved in 6N H_2SO_4) to react with the MnO_2 present in the 25 cc of suspension. (It has been the custom to use 25-50 cc of a sulfuric acid solution of the ferrous salt, made by dissolving 40 grams of the salt in enough 6N acid to make one liter of solution. Hence each 25 cc of the solution contains one gram of the dissolved salt). The soap reacts with some of the acid giving a fatty acid, and perhaps some insoluble iron soap, and the MnO_2 is reduced by the ferrous iron, forming, in the presence of the sulfuric acid, manganese sulfate and ferric sulfate.

It is not necessary to heat the mixture (checked by comparative tests) as is the custom when analyzing pyrolusite, because the suspended MnO_2 is in such a finely divided state that it readily reacts with the ferrous salt. The mixture is diluted to about 250 cc and the excess ferrous salt present is determined by titrating with N/10 $KMnO_4$ solution. In some cases, as will be pointed out later, it may be necessary to filter off the fatty acid before making the titration with the $KMnO_4$.

A blank is run using strengths and volumes of ferrous iron solution and detergent solution equal to that used when determining the amount of MnO_2 in the suspension.

(d) *Calculation of results.* Then we have the simple relation:—cc N/10 $KMnO_4$ for blank *minus* cc N/10 $KMnO_4$ for suspension *equals* cc N/10 $KMnO_4$ equivalent to the amount of MnO_2 present in 25 cc of suspension. Since one cc of N/10 $KMnO_4$ is equivalent to 0.4345 centigrams of MnO_2, the number of cc. of N/10 $KMnO_4$ equivalent to the MnO_2 in 25 cc. of suspension multiplied by 0.4345 gives the number of centigrams of MnO_2 present in that volume, and this value, when multiplied by 40 gives the centigrams of MnO_2 suspended in one liter.

(e) *Expression of results.* The centigrams of MnO_2 suspended in one liter is taken as the "MnO_2 value" of the detergent under the conditions employed. This amounts to practically the same as calling the "MnO_2 value" the number of centigrams of MnO_2 suspended by one kilogram of soap solution under the specific conditions. This is true because, according to McBain,[24] "all soap solutions have approximately the same density as water of the temperature, and this even in extreme concentration"; and because the very minute increase in volume due to suspended MnO_2 is negligible. The use of centigrams eliminates the use of decimals that would be necessary if the values were expressed in grams.

Discussion of the Method and Factors affecting Accuracy

At different times in its development, where MnO_2 was the "dirt" used, the method was put to practical test in the evaluation of some commercial soaps. But time and again disappointment was the writer's portion because, with a given solution, concordant results were not obtained.

In attempting to locate and eliminate the trouble and to obtain concordant results, many experiments were made. Most of these will be dealt with in the following topical discussion of various factors involved in the method. It should be stated, however, that most of these factors would have been involved using any other solid dirt; hence they were not peculiar to MnO_2.

(a) *Reliability of Analysis.* When once the suspension is separated from unsuspended dirt, the method of determining the amount of MnO_2 in suspension, by use of excess ferrous ammonium sulfate in acid solution and subsequent titration with N/10 $KMnO_4$, is very reliable. Using widely differing strengths of suspensions and different kinds of MnO_2 and different soap solutions, this has been checked no less than a dozen times. The analyses of equal volumes of the same suspension always checked within 0.2-0.25 cc of N/10 $KMnO_4$. This is equivalent to an error of less than one percent in the volumes dealt with. This also shows that the provoking discrepancies could not be attributed to grossly faulty technique—pipetting the solutions, making titrations, etc.

That no "side reactions" were taking place which would vitiate this method of analyzing for MnO_2 suspended by soap was shown by (1) determining the effect of various quantities of soap on the titration value of a definite amount of ferrous ammonium sulfate by the $KMnO_4$ solution; (2) determining the effect of various quantities of soap on the titration value of a definite quantity of MnO_2, using one gram of ferrous ammonium sulfate and the stock solution of $KMnO_4$.

For the first experiment, exactly one-gram portions of the ferrous ammonium sulfate were weighed out into separate 500 cc Erlenmeyer flasks. To each was added 50 cc of 6N H_2SO_4 and then 50 cc of either pure water or some soap solution of known concentration. Then the solutions were heated to boiling, diluted to about 250-300 cc. and titrated with $KMnO_4$ solution until a faint pink tinge was apparent throughout the mass of the solution. In some cases, where soap concentration was high, the pink color soon disappeared, but usually the end-point was sharp, though not permanent.

Results obtained from (1) are given in Table III.

This shows that at soap concentrations under one weight-volume percent (this means that where less than 0.5 grams of soap are present, as 50 cc of solution were used) the soap and $KMnO_4$ react to such a small extent that it is negligible. Fortunately, concentrations in which we are interested from a washing standpoint all lie beneath one percent. At increased concentrations there is sufficient soap present so that the unsaturated compounds in it react with an appreciable amount of $KMnO_4$.

TABLE III

Effect of Various Quantities of Soap on the Titration Value of One Gram of Ferrous Ammonium Sulfate with $KMnO_4$

1 gram portions of ferrous ammonium sulfate.
50 cc portions of water or soap solutions.
Solution of $KMnO_4$ slightly stronger than N/10.

Kind of Soap	Percent Conc.	cc $KMnO_4$ to give end point	
Pure water	—	22.4	
Palm Oil	0.2	22.5	
Tallow	0.2	22.5	
Sodium Oleate	0.2	22.4	
Olive oil	0.2	22.4	
Olive oil	0.5	22.5	
Olive oil	1.25	22.8	
Olive oil	2.5	23.2	
Olive oil	5.0	24.0	
Olive oil	10.0	26.0	End point vanished quickly

As a blank is run on the soap solution and ferrous ammonium sulphate any error that might creep in from the above is eliminated. But when dealing with soap concentrations of around 10% the end-point vanishes so quickly as to make it difficult to tell when to stop the titration. To eliminate this the precipitated soap should be filtered off before adding the $KMnO_4$.

(2) By a series of simple experiments it was proved beyond all doubt that the MnO_2 does not in any way react with the soap.

Table IV is included to substantiate the above statement.

TABLE IV

Effect of Various Quantities of Soap on the Titration Value of 0.1 Gram Portions of MnO_2 in the Presence of One Gram of Ferrous Ammonium Sulfate, using $KMnO_4$

0.1 gram portions of C. P. MnO_2.
50 cc portions of pure water or olive oil soap.

Percent concentration	Cc $KMnO_4$ for end-point	
Pure water	22.4	(No MnO_2 was present here)
Pure water	4.05	
0.05	4.00	
0.01	3.95	
0.02	3.90	
0.04	4.05	
0.6	4.1	
0.8	4.1	
1.0	4.15	

It was also demonstrated that there was no impurity in the MnO_2 which was reacting with the ferrous salt or $KMnO_4$.

Therefore, it has been experimentally demonstrated that this method of analyzing for the MnO_2, in the presence of the soap that peptizes it, is reliable and practical, giving a rapid and easy method of determining the amount of "dirt" that a given soap will suspend (peptize or deflocculate) under standard conditions.

(b) *Method of separating True Suspensions from Unsuspended Dirt.* Filtering the unsuspended dirt from the suspended dirt (which goes through the filter paper) was found to be unsatisfactory no matter how it was executed. Allowing the entire 50 cc to drain through or collecting the first 10 cc as did McBain, gave poor results. Some experiments showed 100% difference in the amount of MnO_2 carried through the paper from similarly treated and prepared suspensions. These differences were in all probability caused by the fact that it was impossible to wash the filter paper entirely free of adsorbed MnO_2 which should pass into the filtrate were it not adsorbed by the paper fibers. This in itself would cause erroneous results, but as more and more was adsorbed the pores of the filter paper became clogged and kept back more of the suspended material. There is also a possibility that some of the smallest particles, which had settled out during the period of standing were washed through the filter, provided the soap solution started with was strong enough so that dilution by the wash-water did not immediately reduce the soap concentration below a value where it was affective in carrying MnO_2 through the filter.

Possibly the MnO_2 behaves much worse than the carbon black used by McBain; but we found lamp black just as "unruly" as MnO_2. Separation by centrifuging and subsequent decantation and filtration were tried with no marked improvement in the results obtained.

In laundry practice as well as for a method of analysis, we are interested in the amount of dirt which a given soap solution can peptize or deflocculate or stably suspend, and not in how much dirt it will carry through a given filter paper. Therefore, the method of separation by siphoning off the suspension from unsuspended dirt was attempted. The method went through various stages of development but in the form adopted it is simple, easy to duplicate by any other worker, easy to operate; it is rapid, equally applicable at different temperatures and gives good results as regards separation of true suspension from unsuspended dirt.

At first *equal volumes* of suspension were removed from the different bottles by having the intake of a siphon tube always at the same distance from the bottom of the bottle. Later several experiments were tried in which the intake was always at the same distance from the top of the bottle (by using a 25 cc pipette in a one-holed large cork fixed at a definite position on the stem of the pipette; this cork rested on the "lips" of the bottle when 25 cc of the suspension were being drawn off). These were merely simple means of having the intake at approximately the same distance from the surface of each separate suspension. But in the course of the work one cause of failure

to get concordant results was found to be due to some differences in cross sections of the 100 cc oil sample bottles used. The narrower the bottle, the greater will be the total depth of suspension for equal volumes of liquid. Since MnO_2 is gradually settling out (the rate, according to Stokes's Law, being dependent on the size of the particles) the *total* amount of MnO_2 remaining in suspension, after the lapse of a definite period of time, will be greater, the greater the total depth of the suspension, even though exactly similar suspensions were used at the beginning.

TABLE V

Showing that the Amount of MnO_2 remaining in Suspension in Equal Volumes of a Homogeneous Suspension, varies with the Cross Section of the Container

50 cc portions of a homogeneous suspension.
All stood over night (15-1/2 hrs.) at room temperature.
All were filtered at end of period of standing.
25 cc portions of each filtrate analyzed for MnO_2.
Values given represent the amount of MnO_2, expressed in equivalents of N/10 $KMnO_4$ solution.
Experiments were run in triplicate.

Container used	Total depth of suspension in mm.	MnO_2 suspended in 25 cc expressed in cc $KMnO_4$.	Average
500 cc bottle	15	4.3	
	13	3.7	4.2
	13	4.5	
100 cc bottle	64	6.4	
(oil sample)	65	6.7	6.6
	68	6.65	
Long narrow tubes	562	11.3	
	532	10.6	10.8
	528	10.6	

This is strikingly illustrated by the following experiment where admittedly exaggerated conditions obtained. A liter of a suspension was made by using 20 grams of MnO_2 and 1000 cc of 0.4 percent solution of olive oil soap. The mixture was well shaken and allowed to stand for about an hour. Then about 800 cc were siphoned off from the settled-out material. This was made homogeneous, before removing small aliquot parts, by vigorous shaking immediately preceding the removal of each aliquot part. 50 cc portions of this homogeneous suspension were placed in long narrow tubes or bottles of various sizes. After standing over night, each portion was filtered and then 25 cc of each filtrate were analyzed for quantity of MnO_2 present, using the method already described. It was necessary to separate true suspension from unsuspended material by means of filtration because the wide difference

in total depth of equal volumes of liquid made it impossible to siphon off *equal volumes* of any appreciable value, by having the siphon intake the same distance from the surface of each separate suspension. The results are made clear in Table V.

Hence the removal of *equal volumes,* whether the siphon intake be placed always at the same distance from the surface of the suspension or from the bottom of the bottle, will *not* give concordant results, if the bottles differ appreciably in cross section. But if we remove *all* of the suspension for a definite depth, measured from the surface down, we shall be dealing with equal concentrations, provided the suspensions were similar at the start. Then by subsequent analysis of *equal volumes* of the siphoned-off suspensions we shall obtain concordant results for like suspensions and comparable results for dissimilar suspensions. This is the procedure used in the evaluation of different detergents, to be given later.

It ought to be added here that any method requiring the suspensions to stand for a definite period of time, (however the separation of true suspension from unsuspended material is effected) must be a similar procedure *unless* the vessels in which the suspensions stand are equal in cross section or the dirt used is composed of exceedingly fine particles which settle out very very slowly.

TABLE VI

Showing that the Amount of MnO_2 stably suspended (peptized or deflocculated) increases as Time of Shaking increases

1 gram portions of Kahlbaum Precipitated or Batch B-2 colloid mill MnO_2.

50 cc portions of 0.4% olive oil soap solution.

All mixtures stood at room temperature four hours after shaking.

Siphon method used for separating true suspension from unsuspended material.

Values given represent amount of MnO_2 in 25 cc of suspension, expressed in cc N/10 $KMnO_4$.

Method and Time of Shaking

Colloid Mill MnO_2			Kahlbaum's Precipitated MnO_2			
Hand	Machine	Hand	Machine			
10 sec.	10 min.	10 sec.	2 min.	5 min.	10 min.	20 min.
27.4	30.6	24.4	26.7	29.5	30.4	32.0
26.4	30.2	25.3	26.8	29.5	30.6	31.9
25.4	30.7	24.5	26.0	29.4	30.0	32.7
26.6	30.3	25.2	26.3	29.4	29.6	31.7
26.9	30.3	——	26.0	28.9	29.8	31.4
Av. 26.5	30.4	24.9	26.3	29.3	30.1	31.9

It is important to note that this method can be relied upon to yield a suspension free from unsuspended dirt, unless one is exceedingly careless and stirs up the sediment of MnO_2 when inserting the siphon tube or in the operation of drawing off the suspension. That the suspension is free from unsuspended dirt is shown by the fact that the suspension will pass through a filter paper quite readily. By washing the paper several times only the merest trace of MnO_2 is left adsorbed on the filter paper.

As MnO_2 is very dense (sp. g. 5+) the unpeptized particles settle readily to the bottom. This makes it an especially valuable dirt to use for this procedure. Carbon would not be good to use as the unpeptized particles do not settle readily.

(c) *Method of Shaking*: At first, the bottles containing dirt and detergent solutions were shaken vigorously by hand for about ten seconds. But experiments showed that the amount of dirt taken into suspension by a given detergent was increased by increasing the period of shaking. In general, though not always, more concordant results were obtained by machine shaking for two or three minutes. These facts are well illustrated in Table VI.

This suggests the importance of agitation in washing machines. Undoubtedly deflocculation of the dirt takes place more readily in machines that facilitate thorough agitation.

Since the method and time of shaking the mixture of MnO_2 and detergent solution affects the total amount of dirt stably suspended, the shaking had to be standardized. Shaking by machine can be done more uniformly than shaking by hand. Five minutes was arbitrarily chosen as a convenient and suitable period of shaking, since, as the average values in the preceding table show, after this period of shaking, the amount of dirt that will be suspended, when employing a given soap and a given quantity and kind of dirt, is close to the maximum. Also longer periods of shaking would have necessitated special methods of heating the mixtures during shaking, when working with solutions at temperatures much above that of the room. With the container described on page 813 the heat lost by the mixtures during the five-minute period of shaking was negligible.

(d) *Time of Standing.* McBain and his co-workers,[88] allowed the suspensions of carbon to stand undisturbed 23 hours; then they were shaken vigorously by hand and allowed to stand a further hour before filtering.

In the present work, no more concordant results were obtained when suspensions stood 120, 24, or 15.5 hours than when they stood 4 hours. This latter period was chosen as suitable and convenient and made for economy in working time, as well as ease of temperature control.

When shaken with pure water the MnO_2 all settles out, leaving a clear supernatant liquid, in much less than four hours—usually in less than one hour. Therefore when soap solutions are used, we know that any MnO_2 that remains suspended for four hours or more is due to the peptizing action of the soap that is present in the solution.

(e) *Effect of Different Quantities of Dirt.* When 0.5, 1.0, and 2.0 gram portions of MnO_2 were treated with 50 cc portions of 0.4 percent olive oil

soap and the suspensions analyzed in the usual way, the amounts stably suspended were found to be in practically the same ratio as the amounts of dirt started with. Evidently the ability of the soap to suspend the MnO_2 stably has not been taxed to the limit, in any of the above cases because still more MnO_2 is found to be suspended stably if one used 3.0 grams at the beginning. (But when 4.0 or more grams of the MnO_2 are shaken with the same quantity and strength soap solution, the phenomenon of flakiness and floating occurs and practically no MnO_2 remains in true suspension.) This was the case when smaller concentrations of soap were shaken with one gram portions of MnO_2 and the three other dirts—clay, lamp black, and ferric oxide.

At once one suspects that with, say, one-gram portions of the MnO_2 and 50 cc portions of the 0.4 percent olive oil soap, the suspendible particles are entirely exhausted since about twice as much MnO_2 is stably suspended when two gram portions of the oxide are used. This was carefully checked up three or four times with different kinds of MnO_2 by adding fresh soap solutions to the residues left after siphoning off the suspension. In no case were the suspensible particles exhausted. For example, by three successive exposures of one gram of the colloid mill MnO_2 to fresh 0.4 percent soap solutions, at least 66 percent *more* suspensible particles were found to be present than were suspended by the first 50 cc of the soap—that is, by the regular method of procedure.

Furthermore, by successive exposures of a one gram portion of the MnO_2 to fresh soap solutions (50 cc portions) there was obtained a *total* amount of MnO_2 stably suspended, equivalent to or even greater than the amount suspended by one exposure of a two-gram portion of the dirt to 50 cc of the same soap solution.

One wonders why the soap does not take up at once, that is, on the one exposure as used in the regular procedure, all of the particles it is capable of suspending. Professor Bancroft suggested—what of course seems logical and simple, once it is pointed out to one—that the small particles and the larger particles do not act independently (like a two-phase system) but that the smaller particles are influenced or held back by the larger particles..

Clay was found to act in a manner similar to the MnO_2. It is also interesting to note that McBain and his co-workers[88] found a similar action with the carbon they used. They state that "the carbon residues left on the filter paper from a previous filtration were treated with a fresh sample of the original soap solution to see if any further carbon could be extracted, as there was a possibility that all the fine particles had already been taken through. However the carbon number so obtained was invariably increased many fold. For instance, instead of carbon numbers 0.56, 1.14, 0.88, 1.46, 0.65 and 0.36 there were now obtained such values as 5.01, 3.59, 4.64, 4.39, 5.02 and 4.57 and a third extraction with still further soap still gave quite high results."

Using an amount of MnO_2 that approaches "saturation" of the given soap solution with the dirt, gave no more concordant results than smaller amounts.

For example, three or more grams of MnO_2 with 50 cc of soap solution gave no better results than when one gram was used. The latter amount was retained as the standard amount for determinations made.

Discussion of Phenomenon of Flakiness and Floating of the Dirt. This phenomenon has been mentioned a number of times in the preceding pages.

Working with different kinds of MnO_2, the relative detergent values of different concentrations of the same soap were found to vary somewhat with the kind of MnO_2 used. This was anticipated at the very beginning of this work; but this variation is not peculiar to MnO_2 as a form of dirt. Using the "drop number" method, Hillyer[77] found the relative values of soaps varied with different supplies of kerosene. Papaconstantinou[86] found the protective action of a given soap solution varied with different gold sols and was different for arsenious sulfide sols from that for the gold sols.

With MnO_2 as the dirt, the difference in values between a given soap solution with two different kinds of MnO_2 was more pronounced at low concentrations of soap, i.e., where the ratio of soap to dirt was relatively small—much smaller than is ordinarily met with in practice. For example, with colloid mill MnO_2 the detergent value of a 0.3 percent solution of olive oil soap differs but slightly from that of a 0.15 percent solution. With Kahlbaum's MnO_2 the detergent value of the 0.3 percent solution is what one would normally expect, but with the 0.15 percent solution practically no MnO_2 remains in true suspension. This is because in this latter case flakiness and floating of the dirt occurs, and whenever this happens practically no dirt remains in true suspension. This is true not only of MnO_2 but of other solid dirts as well; e.g., clay, lamp black, and ferric oxide. When working with clay as the dirt, it was found that when the ratio of soap to clay was much less than 1:20 or 25, no good suspensions of clay were obtained but flakiness and floating occurred.

There has not been time to devote to a detailed study of this phenomenon but results obtained during the course of the work show that it depends, in general, upon the soap-dirt ratio, but more specifically upon the ratio of fine particles. The specific volume of the Kahlbaum MnO_2 is 2-3 times as great as that of the colloid mill MnO_2, indicating a larger percentage of fine particles in the former. And with five different commercial soaps, flakiness and floating occurred with higher concentrations of soap when using the Kahlbaum MnO_2 than when using any other kind of MnO_2 or even another kind of dirt.

It is quite possible that the phenomenon of flakiness and floating is due to the exhaustion of soap from the bulk of the solution, due to most of the soap being adsorbed by the dirt which in turn is carried to the interface. And here the dirt is apparently flocculated but instead of falling to the bottom of the bottle, it is held up at the surface of the liquid by entrapped air. Thus there is not left in the bulk of the solution sufficient soap to give an appreciable suspension of dirt. Undoubtedly the solid particles of MnO_2 stabilize the foam* and so the dirt floats at the surface indefinitely. I have samples which have been standing two or three months.

* Bancroft: "Applied Colloid Chemistry", 364 (1926).

That the phenomenon occurs only when the ratio of soap to dirt is relatively low favors such a theory. Furthermore that it apparently occurs more readily the higher the percentage of fine particles also lends support to the theory. *For the greater the surface exposed (per gram of dirt) the greater* should be the adsorption of soap, other things being equal.

It is well known that gelatine is a protective colloid quite similar in effectiveness, in a number of cases, to that of soap. And yet* "years ago Schulze pointed out that small amounts of gelatine solution were as effective as lime or alum in causing the rapid sedimentation of clay and that addition of minute quantities of gelatine to barium sulfate simplified the question of filtration and washing very much". If larger amounts of gelatine are used the flocculation of the clay or many other substances is greatly retarded or prevented. And so we may have a somewhat similar occurrence here when the ratio of soap to dirt is small.

Foaming is a factor in the phenomenon. Saponin, which foams very readily and persistently gave true suspensions of MnO_2 for concentrations of 0.062 to 1.0 percent using, as in the cases discussed above, one gram portions of dirt and 50 cc portions of the solutions. But when the saponin-dirt ratio was about 1:60 flakiness and floating of the dirt occurred just as was found with some soap solutions. Incidentally, 0.5 to 0.125 percent solutions of saponin were found to stably suspend about as much MnO_2 as equal concentrations of soap.

As will be seen in some work to be discussed a little later, temperature is also a factor in this phenomenon of flakiness and floating, which is more pronounced at higher temperatures.

Other detergents, such as silicate of soda, trisodium phosphate and sodium carbonate are capable of peptizing (stably suspending) MnO_2 and other dirts within certain limits of concentration or detergent-dirt ratio. If the ratio of detergent to dirt is too small, we get no true suspension, but neither do we get flakiness and floating. This is because these substances do not foam and therefore no air is entrapped to keep the dirt particles at the top, but instead they soon settle to the bottom. The rate of settling decreases with the increase in concentration of detergent up to a certain value, and then the rate of settling increases as concentration is increased.

It may be added here that the relative detergent values of soaps are not independent of the nature of the dirt used. In other words, specific adsorption obtains here just as in other cases of adsorption.

This may be somewhat disconcerting—though not entirely unexpected—since one cannot measure the relative or absolute detergent values of different soaps, using a given dirt, and then affirm that this relation will hold quantitatively for other dirts. But it should be remembered that qualitative experiments with four different kinds of dirt showed them to be very similar in their action with a given soap solution. What McBain[88] states relative to the carbon black they used holds just as true for the MnO_2 used in our work.

* Bancroft: "Applied Colloid Chemistry", 309 (1926).

McBain says: "The action upon carbon black may be to a certain extent specific and in so far not quite parallel to the effect on oily matter, or on emulsification or on frothing but this would merely limit but not destroy the value of the direct information obtained."

The fact stated above, that 0.5 to 0.125 percent solutions of saponin (which is about the optimum concentration of soap for suspending MnO_2) were found to stably suspend about as much MnO_2 as equal concentrations of soap, is extremely interesting. This information should be of unusual importance to the soap manufacturer for it means that he can add saponin to his soap in large quantities (100% if he so desires) and not decrease appreciably the suspending power of the soap. This does not mean that the resulting soap would be as good a detergent for practical purposes as a soap containing no saponin. There are various other factors to be considered, the more important being the manner in which such a soap would emulsify oils, and the effect it would have upon the skin, and the fabrics. Also there is the possibility that saponin in the presence of soap might act differently than it does alone. This, however, is not likely as it is already used in small quantities as an addition agent in soaps.

At least it opens up a field for investigation which promises to be interesting and useful, and offers the soap manufacturer an "addition product" which is not a mere adulterant but rather a substance, which if thoroughly investigated, might compare quite as favorably with soap for a detergent as the first investigations indicate.

(f) *Other Factors affecting Accuracy of the Method*: For the most part, this method of determining the MnO_2 in suspension checked itself within 2 or 3%. In many cases absolute checks were obtained. The slight variations obtained were to be expected as we are dealing with adsorption phenomena, and not with substances which react in stoichiometric amounts. Such being true it would therefore be rather surprising to have obtained results 100% perfect each time.

There are also two other factors which may have had some bearing upon the fact that it was absolutely impossible to obtain concordant results in all cases.

First, one-gram portions of the dirt may have varied in their content of suspensible particles. But certainly it would be difficult to obtain a more uniform dirt than the one used.

Second, In a few cases the upper limit of "settling-out" material was not characterized by a horizontal plane but by a wavy surface (the upper limit can be observed only in suspensions of low concentration). Thus, there is the possibility of irregular settling. A method of filtering off the unsuspended material before allowing settling to occur in order to eliminate the above, proved useless, giving results which differed by 100%.

(g) *Advantages of the Method here developed using MnO_2 as the Solid Dirt.* It is worth while to summarize the advantages of this method of measuring detergent action and why MnO_2 is so well adapted for this particular problem.

(1) As has already been stated, MnO_2 is a very genuine though not common form of dirt. It forms a real smudge on the skin, clothing, wood work, etc, which cannot be removed with pure water alone, but can easily be removed by the use of soap.

(2) It is insoluble in water and in soap solutions. It is not even attacked by boiling dilute nitric or sulfuric acid. It reacts with ferrous ammonium sulfate, in the presence of sulfuric acid, to give an almost colorless solution.

(3) It can be determined accurately since it reacts quantitatively with the ferrous ammonium sulfate, in the presence of sulfuric acid. The permanganate used in titrating excess ferrous ammonium sulfate is its own indicator. It gives a sharp, distinct end point, although not very permanent in the presence of soap (the decomposed soap-fatty acid).

(4) The particles of MnO_2 that are stably suspended by the soap are small enough so that when the suspension is poured into the acid solution of ferrous ammonium sulfate, the MnO_2 reacts immediately and completely, without the necessity of heating the mixture.

(5) It can be analyzed for in the presence of soap. This has already been explained.

(6) The acid needed for the reaction between MnO_2 and the ferrous ammonium sulfate and between the excess ferrous salt and $KMnO_4$ decomposes the suspension (just what is desired) and also throws the soap out of solution, forming a fatty acid and perhaps a small amount of insoluble iron soap.

(7) By running "blanks" this method can be used equally well with any soap of almost any concentration. The very high concentrations of soap, however, cause the end-point color to disappear rapidly, thus making it difficult to determine accurately the volume of $KMnO_4$ required. But this is true only with concentrations of 5.0 percent and above—concentrations which are very seldom found in practical work and also concentrations which fail to suspend dirt to any appreciable extent.

(8) MnO_2 is suspended stably by dilute solutions of silicate of soda and some other alkali salts and thus there is no difficulty in determining the detergent values of a soap just because it happens to have some such "filler" present.

(9) When once the $KMnO_4$ solutions and the ferrous salt solution, as well as the soap solutions are prepared, one can make two or three score determinations without making any weighings except the one-gram portions of dirt (MnO_2) started with.

(10) MnO_2 is very cheap; it is a common laboratory chemical and the method used for its quantitative determination is rapid.

(11) It has a high specific gravity (5+) which proved to be a real asset in the siphon method of separating true suspension from unsuspended dirt.

(12) The whole method and procedure are simple and rapid. No complicated apparatus or special technique are required. If a thermostat of sufficient size is available it is easy to make 36-40 determinations or measurements in a working day. This includes the entire operation from beginning to end.

(13) The method is entirely practical and has yielded quite satisfactory results in the evaluation (relative) of different detergents.

(h) *A Standard for Testing.* To make it possible for others to employ this method and obtain results comparable to those given by the writer, it would of course be necessary to establish a standard for testing. This has not been done because it would be very difficult to standardize the MnO_2 since different supplies of the oxide would vary greatly in degrees of fineness and this would cause the "MnO_2 value" of a given soap to vary accordingly.

The method could probably best be standardized by determining the MnO_2 value" of a pure soap (synthesized in the laboratory under specified and easily reproducible conditions, e.g., by the addition of the calculated quantity of sodium hydroxide required to react with a definite weight of a designated pure fatty acid). The value of this soap with a given MnO_2, say the colloid mill MnO_2 that has been used in this work, could then be taken as the standard. Then any investigator, using the MnO_2 available to him, could determine the "MnO_2 value" of some of this specific standard soap (which he could easily synthesize), under the same conditions as used in the original standard. The MnO_2 available to him could then be used for evaluating different detergents. By multiplying the "MnO_2 values" thus obtained by a proper factor, (found thus: "MnO_2 value" of standard soap using the MnO_2 available divided by the *standard* "MnO_2 value" of the standard soap) the results should be fairly comparable to those obtained in the present work.

Such a standard has not been made since, in the present work, no pure soap (synthesized in the laboratory) has been used. Further, with the stock supply of colloid mill MnO_2 relative values were obtained which served the desired purpose.

In the present work the main purpose has been to develop a practical method of measuring quantitatively the detergent powers of soaps in order to make a study of fundamental factors in detergent action; also to determine the relative detergent powers of the different soaps furnished by the Palmolive Company. So much time was consumed in developing the method that the study of different factors in detergent action has been curtailed. This study will no doubt be taken up by the next incumbent of the fellowship, who will also no doubt develop a standard for testing.

VI. Application of the Method to the Evaluation of Different Detergents

(A). Sodium oleate and some commercial soaps.
(B). Silicates of soda of different compositions.
(C). Caustic soda and some alkaline salts.

EXPERIMENTAL

(A). Sodium oleate and some commercial soaps.

Materials.

(a) *Dirts.* In practically all of this work the colloid mill MnO_2 was used. In a series of determinations involving different concentrations of sodium oleate the C. P. MnO_2 was used.

(b) *Soaps.* Powers-Weightman "Neutral" sodium oleate was used. Also the Palmolive Company furnished five different kinds of commercial soaps—olive oil, palm oil, tallow, "Green Arrow" and "Green Arrow" containing some silicate of soda. The complete analyses of the last three soaps was not ascertained. The last named contained 5% silicate of soda of the following composition: moisture 63.24%; Na_2O 8.93%; SiO_2 27.83%. These two oxides are in the molecular ratio 1:3.2. The tallow soap was guaranteed to be made from 80% tallow. All three were analyzed for moisture before being used, since solutions were made up on the moisture-free basis.

The following analyses were reported for the olive oil soap and the palm oil soap:

Determination	Olive oil soap	Palm oil soap
Moisture	33.4 %	36.9 %
Titer of fatty acids	18.7°C	44.6°C
Total fatty acid	59.3 %	57.43%
Total alkali as Na_2O	6.7 %	6.49%
Free alkali (Na_2O)	Trace	0.03%
Free caustic as carbonate	0.14%	0.1 %
Free fat	0.25%	Trace
Glycerine	0.7 %	Present
Unsaponifiable matter	3.2 %	1.4 %
Saponification value of fatty acid	195	203
Salt	0.95%	0.93%
Filler	None	None

Procedure.

The relative detergent values of the five commercial soaps listed on the preceding page have been determined for seven different concentrations and at temperatures of 40° and 75°C. With the range of concentrations employed, the values of either side of the concentration that gives maximum suspension of dirt are made available. Comparative values at temperatures less than 40°C were not determined because of the low solubility at room temperature of all but the olive oil soap.

2.0 percent solutions of each soap were carefully made up on the basis of *dry* (moisture-free) soap and the more dilute solutions were made from the 2.0 percent stock solutions by proper dilution. All solutions were fresh or less than a day old. Bottles and dry MnO_2 contained therein always stood in the thermostat long enough to attain constant temperature before the soap solutions, of thermostat temperature, were added. Six bottles at a time were shaken for five minutes and then replaced in the thermostat. After standing four hours (accurately timed) the suspensions were separated from unsuspended material and analyzed as has been described on page 816.

"MnO_2 Values" of different Concentrations of Sodium Oleate.

Before the colloid mill MnO_2 was obtained and while a 15.5 hour period of standing was still employed, a quantitative study of the effect of concentra-

tion was made using the C. P. MnO_2 and different concentrations of the sodium oleate. The determinations were made at room temperature, about 25°C. The results are shown in Figs. 3-5. In obtaining the data for the former, soap concentrations ranging from 0.0312 to 8.0 percent were used, the more dilute solutions being made by progressive dilution of some of the 8.0 percent solution. As the curve shows, the optimum concentration of soap for maximum suspension of dirt is 0.4 percent. A negligible quantity is peptized or stably suspended in concentrations greater than 4.0 percent.

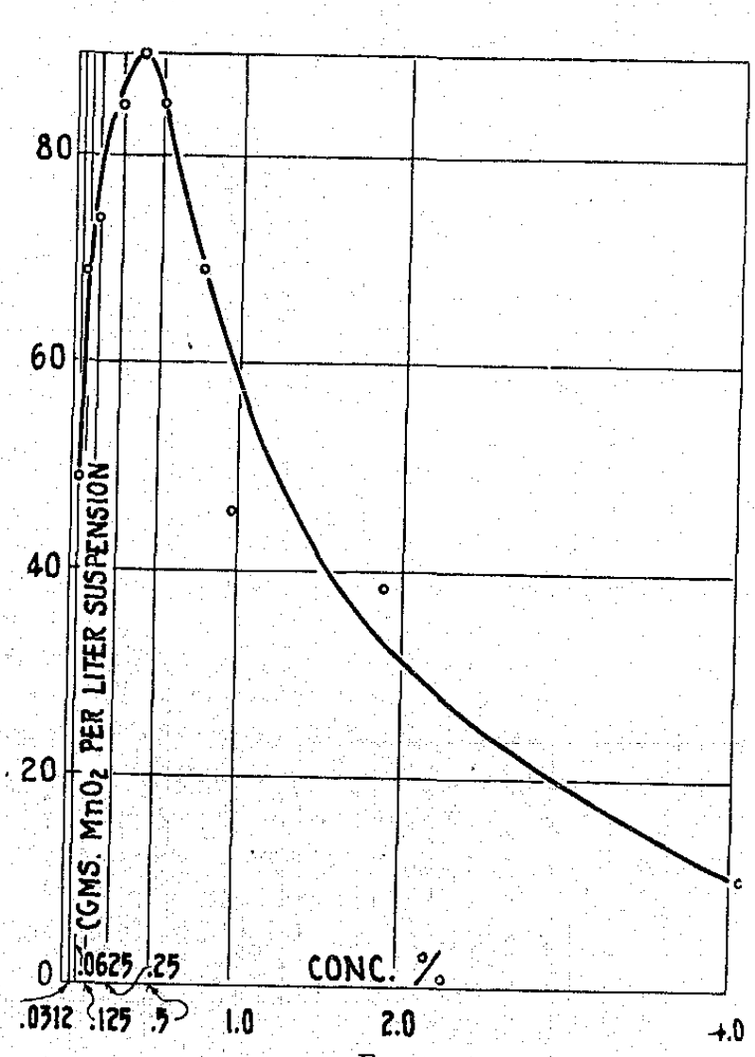


FIG. 3
Sodium oleate.
C. P. MnO_2.
Room temp.

In order to get more specific data for concentrations in the range near the "peak" of the curve in Fig. 3, the value for concentrations ranging from 0.05 to 1.0 percent were determined at intervals of every 0.2 percent. And here the soap solutions were made by weighing out the required amount of the dry powder to make 400 cc of each concentration given. These results are shown in Fig. 4 and here again the "peak" of the curve—the optimum concentration—is for a 0.4 percent solution.

These suspensions not only stood a longer time than in the regular procedure now used, but the C. P. MnO_2 always gave much lower "MnO_2 values" for a given soap than the colloid mill MnO_2. But the relative detergent values of the different concentrations are nevertheless valuable.

In Fig. 5 is shown a similar curve for tallow soap solutions, using the colloid mill MnO_2 and the regular procedure that was used in evaluating all the different detergents.

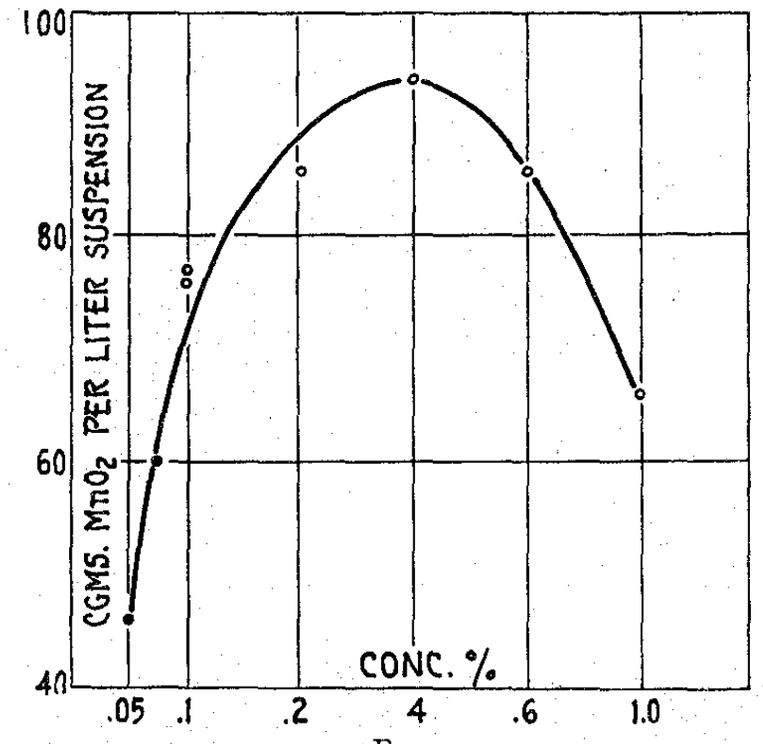


FIG. 4
Sodium oleate.
C. P. MnO_2.
Room temp.

Here the actual "MnO_2 values" are much greater than those given in the first two graphs and the actual values are not comparable with those in the first two (where C. P. MnO_2 was used). But the similarity between the curve in Fig. 5 and that in Fig. 3 is obvious.

These curves are very similar in shape to those obtained by McBain and his co-workers,[88] using carbon as the solid dirt. But, as will be emphasized later, the optimum concentrations are very different in the two cases. They found the optimum concentration about ten times greater than that found in this work.

A more thorough discussion of the "MnO_2 values" will be found, later under "Discussion of Results at 40°C".

Results of Evaluation of the Five Commercial Soaps.

The relative "MnO_2 values" (centigrams of MnO_2 present in one liter of suspension) of the five different soaps for seven different concentrations at 40°C. are given in Table VII. Corresponding values at 75°C. are given in Table VIII.

TABLE VII

Comparison of the "MnO_2 Values" of Various Concentrations of Five Different Commercial Soaps

1 gram portions of Batch B-1 Colloid Mill MnO_2.

50 cc portions of soap solutions.

Values given represent centigrams of MnO_2 present in one liter of suspension as calculated from an analysis of 25 cc of suspension.

Values given are the average of triplicate determinations.

At 40°C

Conc. %	Olive Oil Soap	Tallow Soap	Palm Oil Soap	Green Arrow Soap	Silicated Green Arrow
2.0	412	327	302	387	278
1.4	440	427	377	435	384
0.8	468	496	420	475	486
0.4	453	532	512	522	505
0.2	435	539	550	520	522
0.1	336	328	335	285	323
0.05	162	334	278	320	360

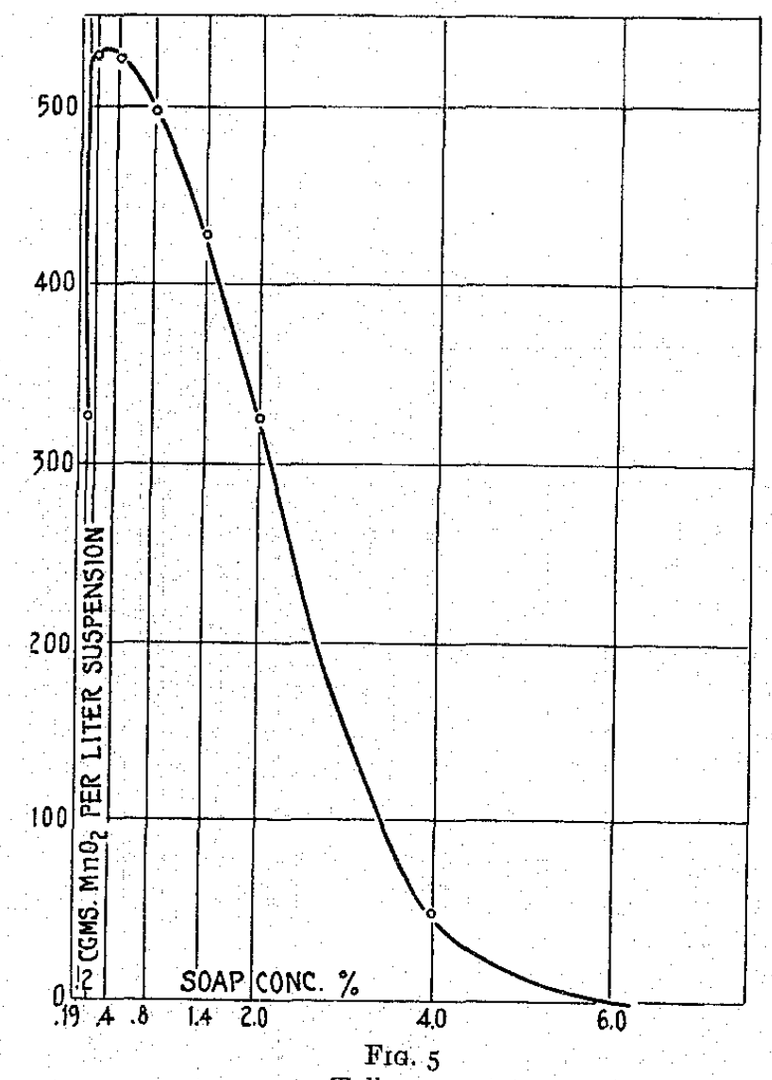


FIG. 5
Tallow soap.
Colloid mill MnO_2.
Temp. 40°C.

TABLE VIII

At 75°C

2.0	322	316	299	325	282
1.4	352	372	342	348	341
0.8	427	433	409	427	416
0.4	453	455	453	448	432
0.2	416	460	455	457	450
0.1	153	322	304	250	261
0.05	85	123	141	134	219

Discussion of Results at 40°C

(a) *Reliability of values.* The values for all of the soaps at 0.05 percent concentrations are not at all reliable, because all gave flakiness and floating. When this occurs the method here used is of little value. It is safe to assume that all of the values for the 0.05 percent concentrations, at this temperature and with this particular MnO_2, are too high. This is true because dirt, not in true suspension, that floats at the top, is mechanically carried over with the small amount of dirt that is in true suspension when the latter is removed from the bottle by use of the siphon tube. All other concentrations gave very consistent and quite concordant values.

(b) *Optimum concentration.* With only one exception, the optimum concentration is in the range 0.2-0.4 percent, with the 0.8 percent a close second. In all cases there is a decided decrease for concentrations below 0.2 percent—the values for 0.1 percent solutions being 25-40 percent less than those for the 0.2 percent solutions.

For one engaged in the business of selling soap it would perhaps be more gratifying to have the optimum concentration in the range found by McBain and his co-workers[88] rather than the low value just reported. Using carbon black as the solid dirt, they found the optimum concentration to be about 4.45 percent. It was stated that adsorption is specific and that two different dirts would no doubt act differently with the same detergent solution. But, as has been stated before, the four different dirts—clay, lampblack, ferric oxide, and MnO_2—all come, qualitatively within the range 0.156 to 1.25 percent of olive oil soap solution for maximum suspension. Judging by turbidity the optimum concentration for suspension of all four was very close to 0.4 percent. Therefore MnO_2 is not an isolated case. Further the values found by the above investigators are much higher than those found by any other investigator whose data has been available.

(c) *Optimum concentration by other workers.* It is interesting to note that Zhuknov and Shestakov[87] found that in laundry practice the best results were obtained with 0.2 to 0.4 percent soap solutions.

Spring,[61] who made only qualitative sedimentation tests with lampblack, ferric oxide and potters' clay found soap solutions of 1.0, 0.5 and 0.03 percent respectively gave most stable suspensions of the three dirts in the order named. Here specific adsorption is distinctly in evidence; but, considering all three kinds of dirt and the optimum concentrations for maximum suspension of each, the range he found agrees much better with the results here reported than with those obtained by McBain and his co-workers.*

Donnan and Potts[64] found an optimum concentration of N/300 (= about 0.6% for the soap they used) in the emulsification of paraffin oil by soap solutions. Shorter[92] says: "A curve showing the relation between 'drop number' and the concentrations of soap solution indicates that so far as surface tension is concerned, it is a waste of soap to use it at a concentration much greater than 0.4 percent." In a very elaborate and involved process for determining the cleansing effect of washing compounds, Heermann,[89] used 0.4 percent soap as the normal concentration for wash experiments. Briggs and Schmidt[79] found 1.0 percent solutions of sodium oleate to be the optimum amount for emulsification of benzene. Papaconstantinou[86] found that 1.0 percent solutions of sodium oleate had slightly better protective action on gold sols than 0.1 percent solutions and the latter, in turn, considerably better than 0.01 percent solutions. From his results—though he gives only three different concentrations—we can deduce the rather wide range of 1.0-0.1 percent solutions for the optimum value. From what I can learn from the laundrymen here in Ithaca, they use perhaps less than 0.1 percent soap solutions. Lenher and Buell,[82] who worked with pure solutions of sodium oleate, found N/320 solutions (equal to about 0.1%) invariably gave maximum suspensions of MnO_2, and ferric oxide.

With the exception of the very high value, 4.45%, obtained by McBain[88] and his co-workers, the optimum concentrations obtained in this work are in fair agreement with those found by other investigators who have attacked the problem in different ways. This very fact strengthens the validity of the method here developed and used, and increases the value of the results obtained.*

(d) *Similarity of all Five Soaps*: At first it was quite a disappointment to find that all five soaps acted so similarly. It seemed that a wide difference in their detergent powers would at least be more impressive and dramatic. But when one considers that "since adsorption is essentially specific, the amount will necessarily vary with the nature of the adsorbing agent, the liquid, and the substance to be adsorbed," it is just as dramatic and no less remarkable that all of the soaps are so very similar in their peptizing action on MnO_2.

The fact that all of the soaps showed practically the same suspending power in the range of maximum suspension led to the suspicion that perhaps the same amount of MnO_2 was suspended by each soap because the suspensible particles were exhausted *before* some of the soaps had exerted their

* Since this was written, Vincent has been able to duplicate McBain's results by varying the time of standing. He will discuss the subject in his thesis.

maximum suspending power. Of course this suspicion would not arise for concentrations above or below the optimum value, since the amount suspended by the latter was always greater than for concentrations above or below it. This was checked carefully three or four times by adding fresh soap solutions to the residues left after siphoning off the suspensions, made by using the optimum concentration of soap. In no case were the suspensible particles exhausted. This has already been discussed.

Since the soaps are similar at equal concentrations, it follows that the optimum concentration will be the same for all, as Tables VII and VIII show (with the exception of the olive oil soap). Here, at a temperature of 40°C, as in many other determinations made while developing and improving this method and analysis, the olive oil soap proved less effective than the other four soaps at the optimum concentration. This was always found to be the case. Also the solutions of sodium oleate always gave values very similar to those of the olive oil soap.

The four saturated fatty acid soaps form gels at ordinary room temperature if the concentration is much in excess of 0.2 percent. Hence there was a possibility that these four soaps might have greater relative viscosities than the olive oil soap at 40°C. If so, this might well account for the larger amount of MnO_2 remaining suspended in them. However, as shown in Table IX, the relative viscosities of 0.4 percent solutions of the five soaps were found to be very similar at equal temperatures. For the sake of comparisons the "MnO_2 values" of the solutions are included in Table IX.

TABLE IX

Relative Viscosities and "MnO_2 Values" of 0.4% Solutions of all Five Soaps at 40°C and at 75°C.

"MnO_2 values" represent centigrams of MnO_2 present in one liter of suspension as calculated from an analysis of 25 cc of suspension.

Relative Viscosities represent time, in seconds, for 5 cc of soap solution to pass between the marks on an Ostwald Viscosimeter. Values given are the average of five determinations.

Soap 0.4% Conc.	"MnO_2 Value" (centigrams)		Relative Viscosity (seconds)	
	40°C	75°C	40°C	75°C
Olive Oil	453	453	64-4/5	39-1/5
Tallow	532	455	66-2/5	39-1/5
Palm Oil	512	453	66	39-2/5
Green Arrow	522	448	66	39-3/5
Silicated G. A.	505	432	66-3/5	39-3/5

As the results indicate, the difference in the "MnO_2 values" of the olive oil soap and the other four soaps can be attributed to difference in viscosities.

By reference to Table VII it will be seen that the olive oil soap apparently excels at the two highest concentrations employed. But concentrations as great as these will seldom be met with in laundry or toilet practice.

(e) *Order of detergent power of the soaps.* It might be parenthetically added here that the reason so much time and effort were expended on improving the method of analysis, already discussed, is because the soaps proved to be so similar. This necessitated refinement of method to increase accuracy of results in order to make it possible for one to distinguish any difference between the soaps. No doubt the four saturated fatty acid soaps differ less among themselves than the limits of accuracy of the method used for measuring their detergent powers. Throughout all the different determinations that have been made, the order of detergent power at 40°C has not always been the same for these four soaps, but they have always exceeded that of the olive oil soap.

Taking the average of all the determinations that have been made, using optimum soap concentration, the order would probably be: tallow ≡ palm oil > Green Arrow > silicated Green Arrow > olive oil. But as noticed above, the difference between the first four is almost negligible. While this is true, it is doubtful if the house-wife would choose the palm oil soap because of the very slow rate at which it goes into solution. This is especially true at 40°C. It dissolves much more slowly than any of the other soaps at this temperature. Once in solution it is as good as any of the others.

Here again it is instructive to compare the results with those obtained by other investigators. McBain and his co-workers[88] used widely different soaps—much more different in composition than the five soaps here used. They say: "Once in solution there is surprisingly little difference between soaps as different as myristate ($C_{13}H_{27}COOK$) and oleate ($C_{17}H_{33}COOK$)". Rasser[74] states: "Different soaps show the following order in cleansing power: tallow; soaps from liquid vegetable oils or olein; cocoanut, palm-kernel, and rosin soaps." Lenher and Buell[82] state, "At 100°C sodium palmitate emulsifies olive oil more efficiently than the oleate or stearate, thus indicating that at 100°C it is a better detergent than oleate or stearate."

From these results by different investigators, it is evident that the order of detergent power varies with the method used to determine it. But all have found the different soaps to be very similar, regardless of the methods used.

(f) *Comparison of Efficiency.* While the optimum concentration for all of the soaps here studied is in the range 0.2-0.4 percent, yet from the standpoint of efficiency the 0.1 percent solutions of soap will win every time, as can be seen from Table VII. That is, the 0.1 percent solutions are capable of suspending considerably more than one-half as much dirt as solutions of two, four, eight or even ten times this concentration. It is quite possible that the 0.05 percent solutions would win in an efficiency contest, but as stated on page 051, the detergent values for this particular concentration are not reliable. Hence any conclusion involving them would be of similar character.

Rasser[74] states that the greatest cleansing efficiency is obtained with 0.2 to 0.4 percent soap solutions. But he is really referring to the best concentration for detergent action. This range is in strict agreement with that found here in this work.

Moreover, it is detergent action in which we are interested. The fact that a 0.1% solution may suspend more in proportion to its concentration than a 0.2% solution does not warrant its use as a detergent. A 0.2 to 0.4% solution is a relatively weak solution anyway, and if it suspends more dirt than a 0.1% it is consequently the solution to use.

Discussion of Results at 75°C

(a) *Reliability of values. The values* have been given in Table VIII. At this temperature the values for the 0.1 and 0.05 percent concentrations are not reliable because flakiness and floating occurred. That this phenomenon did not occur with the 0.1 percent solutions at 40°C but did at 75°C is evidence that not only soap-dirt ratio or soap-fine-particles ratio is a factor but that temperature also is a factor in producing flakiness and floating.

(b) *Optimum concentration and similarity of soaps.* Here, as at 40°C, the maximum suspending power of the soaps is exerted when concentrations are in the range 0.2-0.4 percent, although again, the 0.8 percent solutions give only slightly less values. The 0.1 and 0.05 percent solutions have detergent powers decidedly less than the 0.2 percent solutions but just how much less, cannot be determined by the values given in Table VIII, since, for these more dilute solutions, the values are not reliable.

Also at this higher temperature the five soaps are very similar, with the similarity being perhaps more striking for the concentrations 0.2 and 0.4 percent than it was at 40°C.

(e) *Effect of temperature.* For equal concentrations of soap solution the detergent values at 75°C are less than at 40°C. This is true of all five soaps at the seven different concentrations except the 2.0 percent solution of silicated Green Arrow.

To show that the decrease, where MnO_2 is the dirt, was not due to a more or less sintering or stable agglomeration of the MnO_2 particles at this higher temperature, several bottles of the one-gram portions of dry MnO_2 were kept at a temperature of 75°C for over four hours. After this they were allowed to cool to 40°C and suspensions were made with a detergent at this temperature. The amount of MnO_2 suspended was practically no different from that found when the MnO_2 had not been warmed up to a temperature above 40°C and the same detergent solution used. Thus the difference in detergent powers, at different temperatures, for equal concentrations of a given soap, must be due to changes in the properties of the soap itself.

This decrease in detergent power, as temperature increases, comes somewhat as a surprise until we consider some of the factors involved. Hillyer[7] showed experimentally that emulsifying and wetting properties of soap solutions, both of which are factors in detergent action, must be due to soap itself. He states: "Low surface tension and emulsifying power are due not to the alkali or to acid set free by hydrolysis but to undecomposed soap itself."

(d) *Results by other investigators.* Hillyer found the "drop number" of rosin soap of all concentrations from N/10 to N/320 to be less at 100°C than

in the cold. This decrease was accounted for on the basis of hydrolysis. The latter increases with temperature and this would mean *less* undecomposed soap for a given concentration at 100°C. than at room temperature. And he accounted for the decrease in "drop number" on the basis of the decrease in amount of undecomposed soap for a given soap solution. If this be true, the results obtained by the use of MnO_2 as the dirt fit in very well.

In the very inclusive article, "Colloid Chemistry of Soap", McBain[24] says that soap solutions are much more colloidal at lower temperatures than at the boiling point. He also states that the detergent action parallels the amount of colloidal soap present. Later, in actual measurement of detergent action, using a solid dirt, McBain and his co-workers[88] found that increase of temperature greatly diminished the "carbon number" of the soaps they used—potassium oleate and potassium myristate. With the latter, they found 30 percent less carbon suspended at 60°C than at 25°C.

On the other hand, Papaconstantinou[86] found the protective action of soaps on gold sols to increase with increase in temperature. Curiously enough he makes use of the conclusions of McBain[24] to account for this action; but he gives an interpretation which has little meaning—to me at least. He says: "McBain and his co-workers, from a study of the lowering in vapor-pressure and the electrical conductivity, have concluded that the ionic micelles of the soap decrease in size with rise in temperature. The increase in mobility (and possibly in number) of the ionic micelles with rise of temperature together with the increase in thermal agitation of the soap micelles and the gold particles may therefore be connected with the increase in protective action (viewed from a kinetic standpoint)." Then he adds: "If we adopt the theory of Spring, that the washing power of a soap is related to its power of forming 'adsorption compounds' with the dirt particles, it is probable that the relative washing powers of soaps will be connected with their relative protective actions toward a gold sol."

Undoubtedly there is a parallelism between the detergent powers of soaps and their protective action on gold sols, but to what limits or extent this parallelism may be said to hold, is, to some extent at least, a matter of opinion as well as a question requiring still more experimental evidence.

We must admit that the method used by Papaconstantinou[86] does not give results analogous to those obtained by Hillyer[7], by McBain and his co-workers[88] or to those obtained in the present work. Since the measurements by Papaconstantinou did not involve any form of dirt, while those by the other three involved either a liquid or a solid dirt, it is natural to give more weight to the latter.

In some emulsification experiments, Lenher and Buell[82] found that a definite amount of sodium oleate would emulsify more of an oil at high temperature, than at low; but that the emulsions were not so stable at the higher temperature. This would seem to lend some support to the results obtained by Papaconstantinou, but it is not in agreement with the results obtained by Hillyer who was using a liquid dirt.

Based on the results herein reported we can say that, once in solution, the detergent powers or the suspending powers of all five soaps toward the dirt MnO_2 is better at 40°C than at 75°C. Where olive oil soap was used at room temperature, the detergent power was found to be greater than at 40°C. In view of this work and that of some others noted above, we are justified in drawing a more general conclusion, viz., that if soaps are once in solution, their detergent powers are decreased rather than increased by rise in temperature. However, the saturated fatty acid soaps will never be in demand for cleansing agents at room temperature, because of the slow rate at which they go into solution as well as their low solubility at this temperature.

Résumé of Relative Values of the Five Soaps

We may summarize as follows concerning the relative detergent action of the five commercial soaps used:—

(1) There is an optimum concentration (0.2-0.4%) for which the suspending power toward MnO_2 is a maximum.

(2) This range for optimum concentration is the same for all five soaps—with the olive oil soap a slight exception.

(3) The optimum concentration is the same at the different temperatures used—75°, 40° and room (=25°C).

(4) All five soaps are surprisingly similar in suspending power at the same temperature and at equal concentrations, except the olive oil soap which is somewhat less effective than the other four soaps.

(5) Increase in temperature from 40° to 75°C diminishes the suspending power of all five soaps, an average of about 20 percent. This is equivalent to a decrease of 0.5 to 1.0 percent per degree rise in temperature, at the optimum concentration.

(B) *Evaluation of Different Kinds of Silicate of Soda*

Different investigators have made various claims for the effect of "addition agents" on the detergent powers of soaps. Most of the experimental evidence has been obtained by determining the effect on surface tension of soap solutions produced by adding a base or an alkaline salt. That "addition agent" which produces the greatest lowering of the surface tension of a given soap solution has been assumed to enhance the detergent power of the soap the most.

The quantitative method of measuring detergent action developed in this work makes possible the evaluation of these different agents alone as well as soap solutions containing them.

Materials and Procedure

This work shows that silicate of soda solutions act similarly to soap in suspending MnO_2 stably. Samples of this so-called soap filler of various compositions were furnished by the Philadelphia Quartz Company. The three brands used were designated by letters and had the compositions shown in Table X.

The relative detergent values of nine different concentrations were determined at 40° and at 75°C, in a manner exactly similar to that used in

evaluating the soaps. Fresh 0.5 percent stock solutions were made up on the basis of Na_2O, SiO_2 content. The more dilute solutions were made by proper dilution of a known volume of the 0.5 percent stock solutions. The "MnO_2 values" are given in Table XI.

TABLE X

Composition of Silicates of Soda used

Brand	Sp. Gr.	$\%Na_2O$	$\%SiO_2$	Ratio Na_2O : SiO_2 Percent Molecular	
"S"	1.31	6.4	24.7	1 : 3.86	1 : 3.97
"K"	1.48	11.0	31.2	1 : 2.84	1 : 2.92
"BW"	1.68	19.4	30.6	1 : 1.58	1 : 1.62

TABLE XI

Comparison of the "MnO_2 Values" of Various Compositions of Three Different Silicates of Soda at 40° and at 75°C

1 gram portions of Batch B-2 Colloid Mill MnO_2

50 cc portions of silicate of soda solutions

Values given represent centigrams of MnO_2 present in one liter of suspension as calculated from an analysis of 25 cc of suspension. These values are the average of duplicate determinations.

Conc. %	"S" Brand 40°C	"S" Brand 75°C	"K" Brand 40°C	"K" Brand 75°C	"BW" Brand 40°C	"BW" Brand 75°C
0.5	292	240	219	205	40	61
0.3	382	261	316	247	219	200
0.15	396	287	394	300	396	300
0.05	434	346	430	342	431	344
0.025	445	351	431	342	452	348
0.0125	436	348	433	334	437	313
0.0062	427	216	297	247	404	227
0.0031	278	000	41	000	203	38
0.0015	36	000	000	000	19	000

Discussion of Results

(a) *Reliability of values.* Except for a few erratic results for the two lowest concentrations, these values are reliable. However, they are not exactly comparable with those in Tables VII and VIII, pp. 832-833, since Batch B-2 MnO_2 gave values about 4.0 percent higher than Batch B-1, with the same kind and concentrations of detergent solution.

(b) *Similarity of action of silicate of soda and soaps.* The similarity between the action of silicate of soda solutions and of soap solutions is very striking. Thus for relatively high or low concentrations, very little MnO_2 is stably suspended. There is an optimum concentration range, within which the values for different concentrations of the same silicate differ but little. For the silicates the optimum concentration range is 0.0125-0.05 percent, whereas for soaps it is 0.2-0.4 percent. The optimum concentrations of all

the silicates have "MnO_2 values" numerically less than all the soaps. This is true for both temperatures. But the values at 40°C approach very closely to those for olive oil soap at the same temperature.

(c) *Effect of composition of the silicate.* There is a very marked difference between the values for "S" brand and those for "BW" brand in the 0.5 and 0.3 percent solutions, while the "K" brand has values intermediate between these two extremes at these same concentrations. But the values for all three silicates differ only slightly within the optimum range of concentration.

By reference to Table X, it will be seen that the "S" brand is high in silica, the "BW" is low in silica (= high in alkali), while the "K" is of a composition intermediate between these two. As just indicated, there is a corresponding difference in "MnO_2 values" for the higher concentrations. At concentrations greater than 0.15 percent, the more siliceous (= less alkaline) silicate is distinctly superior to a highly alkaline silicate, for suspended MnO_2. These results make it easier to understand the conspicuously contradictory results obtained by different investigators—Richardson,[84] Stericker,[71] Millard[83] and others—who have studied the detergent action of silicate of soda. In the first place, different men worked with silicates unlike in Na_2O-SiO_2 ratio and in the second place, some worked with only one concentration of silicate of a particular composition and this was probably too high.

Using concentrations of 0.5 percent and greater, Stericker[71] found that mineral oils (kerosene, Acto, U. S. P.) were more readily emulsified by silicates in which the ratio of silica to soda is relatively high. If emulsification of oils parallels the peptization of MnO_2, then the results obtained with this dirt are in exact accord with Stericker's (for the one common concentration, viz. 0.5 percent). For solutions still more dilute, e.g., within the optimum concentration range (0.0125-0.05%), there is little choice between the different silicates as regards their peptization of MnO_2.

Millard[83] found that an alkaline silicate of soda produced a greater decrease of surface tension when added to a 0.03 percent soap solution, than when a less alkaline silicate was added. He was working with silicate of soda solutions of concentrations ranging from 0.012-0.139 percent and so was within the range found here for maximum suspension of MnO_2. The maximum values I obtained are so very similar that it does not seem justifiable to claim superiority for any one particular brand, *when used at the optimum concentration.* However, it would seem advisable to use a silicate high in SiO_2, for it is indeed superior unless the concentration is kept below a certain value. Furthermore, the initial cost should be less than a silicate high in soda.

(d) *Effect of temperature.* Just as rise in temperature was found to decrease the suspending power of the soaps, so also a similar effect was observed when silicate of soda alone was used. Other things being equal, this means that silicate of soda is more advantageous in a cold water soap than in a hot water soap. Within the range for maximum suspension of MnO_2 the silicates are about 22-25 percent more effective at 40°C than at 75°C, and they have been found to be about 12-15 percent more effective at room temperature than at 40°C.

(e) *Silicate of soda as a detergent.* If this suspending power or peptizing power of a substance toward MnO_2 is to be taken as a measure of detergent action (and we believe it is, as has already been explained), then the results here obtained are added evidence to the claims made by Stericker[71] and others, viz., that silicate of soda is more than a mere filler for soaps; it has detergent properties of its own. It is significant that he showed this to be true for liquid dirts, whereas the present work has demonstrated it to be true for a particular solid dirt, MnO_2. No quantitative measurements have been made, but qualitative tests showed that silicate of soda solutions are capable of suspending other solid dirts, clay and lampblack, as well as different kinds of MnO_2. The effect of the silicate of soda on the fiber that is washed in a silicated soap is still an open question.

By far the most important result which is arrived at from this investigation of silicate of soda is that it is not just a "tolerant" filler for soaps but that it is an exceptionally good addition agent.

Before we can be definitely certain that it is advisable to add silicate of soda to soaps in large quantities it's effect on emulsifying oils and on the fabrics and skin must be investigated. But silicate of soda might be added to soap until it forms nearly 100% of the cake without greatly decreasing the suspending power of the soap.

Using the values for the "S" brand sodium silicate, which appear best, a 0.3 percent solution at 40° has almost 85% suspending power of olive oil soap, and 72% the suspending power of tallow soap.

Certainly this fact should cause the heart of every soap manufacturer to beat in wild ecstasy. It is not advised that the manufacturer should start immediately to place a highly silicated soap (approximately 100%) on the market. Before this is done the problem must be further investigated. But no one can now say that such and such a soap is highly adulterated with sodium silicate, for sodium silicate is not an adulterant but rather a detergent. Further investigations may prove that a high content of sodium silicate is desirable from various other standpoints.

We are deducing from the fact that sodium silicate alone shows a detergent action on solid dirts comparable to soap that it can be added in large quantities to soap. Experiments in which varying amounts of the soap have been replaced by sodium silicate should be made.

(C) *Evaluation of Caustic Soda and Some Alkaline Salts.*

Action of different alkalies on different dirts.

"Addition agents" other than silicate of soda such as sodium carbonate, borax, sodium hydroxide are often present in some soaps. As experiments of last fall showed, silicate of soda acted very similar to soap in suspending the MnO_2 used (stock-room supply), but sodium carbonate, borax and sodium hydroxide failed to stably suspend the MnO_2.

But later, these same substances as well as trisodium phosphate were found to peptize the colloid mill MnO_2, if the concentrations were not too

strong or too weak. This was true of all except the borax which failed to peptize either kind of dirt even though a wide range of concentrations was employed.

The earlier experiments differed from those of later date only in the kind of MnO_2 used and the method and time of shaking the mixtures of dirt and solutions. Experiment has demonstrated that the results obtained earlier, with the stock room supply of MnO_2, were correct. Shaking the mixtures of this dirt and these different alkalies in the machine for five minutes made no difference. The dirt settled out as quickly from the alkaline solutions as from pure water. Only silicate of soda and soap solutions produced stable suspensions.

With the colloid mill MnO_2 all of these solutions, except the borax, gave good suspensions. The difference in action of these alkaline solutions on the colloid mill MnO_2 cannot be attributed to contaminations of the latter with some oil or organic acid, which then reacted with the added alkaline solution to produce a soap, which in turn peptized the dirt, because borax was no more effective than pure water.

Other dirts—clay, lampblack, C. P. MnO_2, and Kahlbaum MnO_2—were subjected to the action of these solutions. Only qualitative tests were made, but all gave fairly good suspensions except the borax and C. P. MnO_2.

This is another illustration of the specificity of adsorption and emphasizes fineness of particles as an important factor. Since soap and silicate of soda were able to peptize the untreated MnO_2, and these other alkaline solutions were not able to do so, the former must be more powerful peptizing agents. This is shown to be true in a quantitative way, Table XII. One may attempt to explain the difference by saying that silicate of soda and soap have greater ability to disengage strongly agglomerated particles; it hardly seems plausible that these solutions could break up single large particles into smaller, suspending particles, as one might break a stone into smaller pieces with a hammer or with a mortar and pestle. But when the dirt was put through the colloid mill the particles were decreased in size and the number of fine, suspensible particles was increased so that the weaker peptizing agents (caustic soda and the alkaline salts already mentioned) became effective. One wonders why the borax was ineffective toward the colloid mill MnO_2 and yet was able to peptize the Kahlbaum MnO_2.

The property common to caustic soda, sodium carbonate, trisodium phosphate and borax is that their aqueous solutions have an alkaline reaction due to excess of hydroxyl ions. Their peptizing action is due no doubt to adsorption of these hydroxyl ions by the solid particles of dirt. If this is the explanation, it is difficult to see why borax "acts so stubbornly" in some cases. Possibly the borate ion or the weakly ionized boric acid exerts a counter effect in some cases.

The "MnO_2 values" of various concentrations of the alkalies named in the preceding paragraph have been determined just as they were for soaps and the silicates. The values are given in Table XII. For the sake of comparisons, the values for "S" brand silicate of soda are added, Table XI. No values for borax are included since it formed no stable suspensions.

TABLE XII

Comparison of the "MnO_2 Values" of Various Concentrations of Different Alkaline Solutions at 40°C and at 75°C.

1 gram portions of Batch B-2 Colloid Mill MnO_2.

50 cc portions of alkaline solutions.

Values given represent centigrams of MnO_2 present in one liter of suspension as calculated from an analysis of 25 cc of suspension. These values are the average of duplicate determinations.

Conc. %	"S" Silicate 40°C	"S" Silicate 75°C	NaOH 40°C	NaOH 75°C	Na_2CO_3 40°C	Na_2CO_3 75°C	Na_3PO_4 40°C	Na_3PO_4 75°C
0.5	292	240	000	000	000	000	000	40
0.3	382	261	000	000	000	000	000	140
0.15	396	287	17	52	000	12	70	274
0.05	434	346	232	231	30	99	350	290
0.025	445	351	347	269	110	196	365	291
0.0125	436	348	373	252	284	234	273	248
0.0062	427	216	333	140	203	140	125	113
0.0031	278	000	17	000	68	17	40	000
0.0015	36	000	000	000	000	000	000	000

Discussion of Results

(a) *Reliability of values.* In some cases erratic results were obtained, especially with the Na_3PO_4 but these determinations were repeated. So, in general, the values are fairly reliable. Where the figures "000" occur, the suspensions became clear in less than four hours and hence there was no MnO_2 to analyze for.

(b) *Optimum concentration.* For all of these substances there is a rather narrow range of concentrations that will give stable suspensions. It is much more limited than where soaps or silicates are used. There is an optimum concentration for each in the range 0.0125-0.025 percent. In almost all cases suspending power decreases with rise in temperature, and in this respect they resemble the soap and silicate solutions. There is not very much difference between the effectiveness of the sodium hydroxide solutions and equal concentrations of the trisodium phosphate. This is to be expected since the latter salt is 100 percent hydrolyzed in aqueous solutions. There is some difference at the higher concentrations and at the higher temperature. This may be due to the influence of the relatively weak acid anion, HPO_4'', formed by hydrolysis of the normal salt, but if this is the case, its effect is apparently negligible in the range of optimum concentration. Sodium carbonate is less effective than the other two alkaline substances.

As has already been indicated, silicate of soda solutions and soap solutions are better peptizing agents for this particular dirt than are these alkaline solutions.

(D). *Evaluation of Mixtures of Soap and "Addition Agent."*

Among those who have claimed that "addition agents" lower the surface tension of soap solutions, and thereby enhance the detergent action of the

latter, are Richardson,[83] Elledge and Isherwood,[78] and Millard.[83] The latter found the reducing effect of different agents on the surface tension of a 0.03 percent solution of soap, to be in the following order:—sodium hydroxide > sodium carbonate > trisodium phosphate > "BW" silicate of soda > modified soda > "Star" silicate. He states: "The decrease in surface tension produced by an "addition agent " when a soap solution of mixed concentration is used, has been considered a measure of the cleansing power until some more definite way of measuring this property is established."

Experiments show that this cannot be taken as a true criterion. Hillyer[7] showed that surface tension is reduced continuously with an increase in concentration of the soap solution, whereas the emulsifying power of such solutions increases with concentration only up to a certain point (a little less than 2.0%) and subsequently decreases. So also Harkins and co-workers[66] found the surface tension of sodium oleate solutions against benzene decreased as soap concentration increased up to N/10 solution (=3.13%). Briggs and Schmidt[24], however, found the optimum amount of sodium oleate for the emulsification of benzene to be 1.0 percent solution, and Donnan and Potts[64] found an optimum concentration of about 0.6 percent solution in the emulsification of paraffin oil by soap solutions. In the present work 0.2-0.4 percent solutions of soap have been found to give maximum suspension of different dirts, although according to the experiments of Hillyer and Harkins just mentioned, the surface tension of these solutions is appreciably higher than that of more concentrated solutions. Thus it does not seem justifiable to claim that a solution with the lowest surface tension will have the greatest detergent power.

Referring to Tables VII and VIII, it will be seen that we can increase the detergent value of soap solutions of 0.1 and less percent concentration by adding more soap, that is, by making a 0.2 or 0.4 percent soap solution. But we cannot increase the detergent power of a 0.4 percent solution by adding more soap, say sufficient to make a solution of 0.8 or greater percent concentration. But in *all* of these cases, as we add soap to soap, we are lowering the surface tension of the original solution.

Since soap itself is a better detergent than any "addition agent", and since soap added to a soap solution already at its optimum concentration for cleansing power, does not enhance the cleansing power of the solution (but does decrease its surface tension), we should not expect an "addition agent" to enhance the cleansing action of a soap solution unless the latter was at a concentration *less* than its optimum value. Unless this latter condition obtains, the criterion used by Millard[83] goes by the board. This was found to be the case in actual experiment.

The two papers by Chapin[93] were published after this work was finished and written up, so that a discussion of them is not included.

Summary

(1) A brief history of soap industry has been given.

(2) A résumé of various factors suggested by different investigators as entering into detergent action, has been given in chronological order.

(3) A summary of the methods that have been used for measuring detergent action of soaps has been given.

(4) The method developed by McBain and his co-workers has been described and some serious objections to the method of procedure have been pointed out.

(5) A theory of measuring detergent action as proposed by Dr. Bancroft has been given.

(6) Qualitative tests showed the optimum concentration of olive oil soap or sodium oleate solutions, for suspending a fine grade of clay, to be in the range 0.156-0.625%.

(7) The same range holds true for at least three other kinds of solid dirt—lampblack, ferric oxide, and manganese dioxide.

(8) The soap-dirt ratio, or more specifically the soap-fine-particles ratio is of importance in obtaining suspensions of dirt in the detergent solution. If the ratio of soap to dirt is less than 1:25-30 (a condition seldom, if ever, met with in laundry practice) practically no dirt is stably suspended, but "flakiness and floating" occur. An explanation of this phenomenon has been offered.

(9) The method of estimating the cleansing power of soaps by the use of sodium chloride, or a number of other salts, on suspensions of clay in soap solutions, was found not to be feasible.

(10) A practical method has been developed for the direct and rapid determination of the amount of finely divided MnO_2 which various detergent solutions are able to suspend for a definite period of time. This gives an "MnO_2 value" characteristic of each solution which may be taken as a measure of the detergent value of the material tested.

(11) The method of procedure has been outlined and a discussion of the method and factors affecting accuracy of results obtained by it has been given.

(12) The advantages of this method have been emphasized.

(13) Practical application of the method has been demonstrated in the evaluation of (a) sodium oleate and some commercial soaps, (b) silicates of soda of different compositions, (c) caustic soda and some alkaline salts, mixtures of soap and "addition agents."

(14) The relative detergent values of soaps differ with different dirts, due to specificity of adsorption.

(15) The relative detergent powers of various concentrations of five different commercial soaps—olive oil, palm oil, tallow, "Green Arrow" and silicated "Green Arrow"—have been determined at 40°C. and at 75°C. There is an optimum concentration for all five soaps, at both temperatures, in the range of 0.2-0.4 percent. The four saturated fatty acid soaps are surprisingly similar at the same temperature and at equal concentrations. Olive oil soap solutions are less effective than these four at the optimum value. The detergent values of all the soaps decrease with increase in temperature.

(16) A comparison of the results obtained here with those obtained by other investigators has been given.

(17) Solutions of silicate of soda are similar to soap in their ability to peptize different solid dirts. There is an optimum concentration for all the silicates in the range 0.0125-0.05 percent. At concentrations greater than 0.15 percent the silicates relatively high in silica greatly excel those high in soda in their ability to peptize solid dirts. The detergent powers of the silicates are less than the soaps at the optimum concentration of each. Just as with soaps, the detergent action decreases with rise in temperature.

(18) Caustic soda, sodium carbonate, and trisodium phosphate solutions are able to peptize some kinds of MnO_2 but not others. Where they act as suspending or peptizing agents, the optimum concentration for maximum suspension is in the range 0.0125-0.025 percent. Increase of temperature also decreases the suspending power of these solutions.

(19) Maximum surface tension lowering is not a safe criterion for estimation of maximum detergent action. "Addition agents," even though they may lower the surface tension of soap solutions, will *not* enhance the detergent action of soap solution towards MnO_2, if the soap is at or above the optimum concentration. If the original soap concentration is less than the optimum value, an "addition agent" (if it itself is able to peptize the dirt) will increase the detergent power of the original soap solution for the reason that they act like soap and adding them is equivalent to adding more soap, thus bringing the total detergent content of the solution nearer to the optimum.

(20) Silicates of soda, as "addition agents" to soap solutions whose concentrations are *below* the optimum value, enhance the detergent powers of the soap more than other alkalies, such as sodium hydroxide, sodium carbonate, and trisodium phosphate because silicate of soda is more nearly like soap than the others.

(21) As saponin, and sodium silicate ($Na_2O_1SiO_2$ = 1 : 3.86 approximately) have almost as much power as soap to suspend MnO_2 it should be possible to use them in exceedingly large amounts (approximately 100%) as a substitute for soap in the original cake.

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The writer feels greatly indebted to Professor Bancroft, under whom this work was carried out for the interest, helpful criticisms, and encouragement manifested throughout the work.

The writer is glad to make known in this more public way his appreciation of the help and encouragement received throughout this work from his wife, Dorothy J. Fall.

Cornell University

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HEATS OF IONIZATION IN METHYL ALCOHOL

J. H. WOLFENDEN, W. JACKSON AND H. B. HARTLEY

The object of the work described below was the determination of the heat of neutralization of methylates by acids in methyl alcohol solution, as a contribution to the general study of the electrochemistry of methyl alcohol solutions being pursued in this laboratory. In the simplest case, the neutralisation of a strong acid like hydrogen chloride by a strong base like sodium methylate, the predominant reaction is the formation of methyl alcohol by the union of hydrogen and methoxy ions according to the equation

$$H^{\cdot} + CH_3O' = CH_3OH$$

and measurement in dilute solution should give an approximate value for the heat of ionisation of methyl alcohol. When either weak acids or weak bases participate in the reaction, complications arise which will be discussed later. Measurements were carried out in an adiabatic calorimeter designed for the purpose and extended over a range of concentration. The acids used were hydrogen chloride, hydrogen bromide, acetic and salicylic; the bases, sodium methylate and methyl alcohol solutions of ammonia and aniline.

Experimental

Apparatus. The general arrangement of the calorimeter is illustrated in the two diagrams. The basic solution is run in from the jacketed glass vessel A into a silver calorimeter B, of 650 cc. capacity, containing the acid solution. The calorimeter is supported by corks, leaving an air-gap of 1 cm., in a liquid-tight brass submarine C completely immersed in a paraffin bath to which heat is supplied electrically to maintain the adiabatic condition. The heat capacity of the system is then measured by the supply of a known quantity of electrical energy to a glass-sheathed coil D immersed in the calorimeter liquid. Temperature measurements are made on two standardised Beckmann thermometers F,F.

The calorimeter liquid is stirred by a silver stirrer G of the Richards type connected through thermally insulating vulcanite rods with a system of yokes and bearings H causing it to move up and down through the liquid at about sixty strokes per minute. The stirrer for the basic liquid is a glass spiral L of diameter almost half that of containing vessel. The paraffin bath M is stirred by a propellor N consisting of some fifteen twisted copper vanes disposed spirally about a vertical steel rod. The temperature of this bath is controlled by a heating coil of nichrome wire and a cooling coil of copper tubing through which a stream of cold water may be passed. Both were situated under the submarine at M and the propellor stirrer making 450 revolutions per minute ensured a rapid and uniform heat distribution. To ensure approximate equality of temperature of acid and alkali at the time of mixing, paraffin is

circulated between the outer vessel of the calorimeter and the jacket of the alkali vessel by means of a rotary pump at a rate of about three-quarters of a gallon per minute.

The electrical calorifer. The convenient method of electrical calibration, introduced into adiabatic calorimetry by McInnes and Braham[1], has many

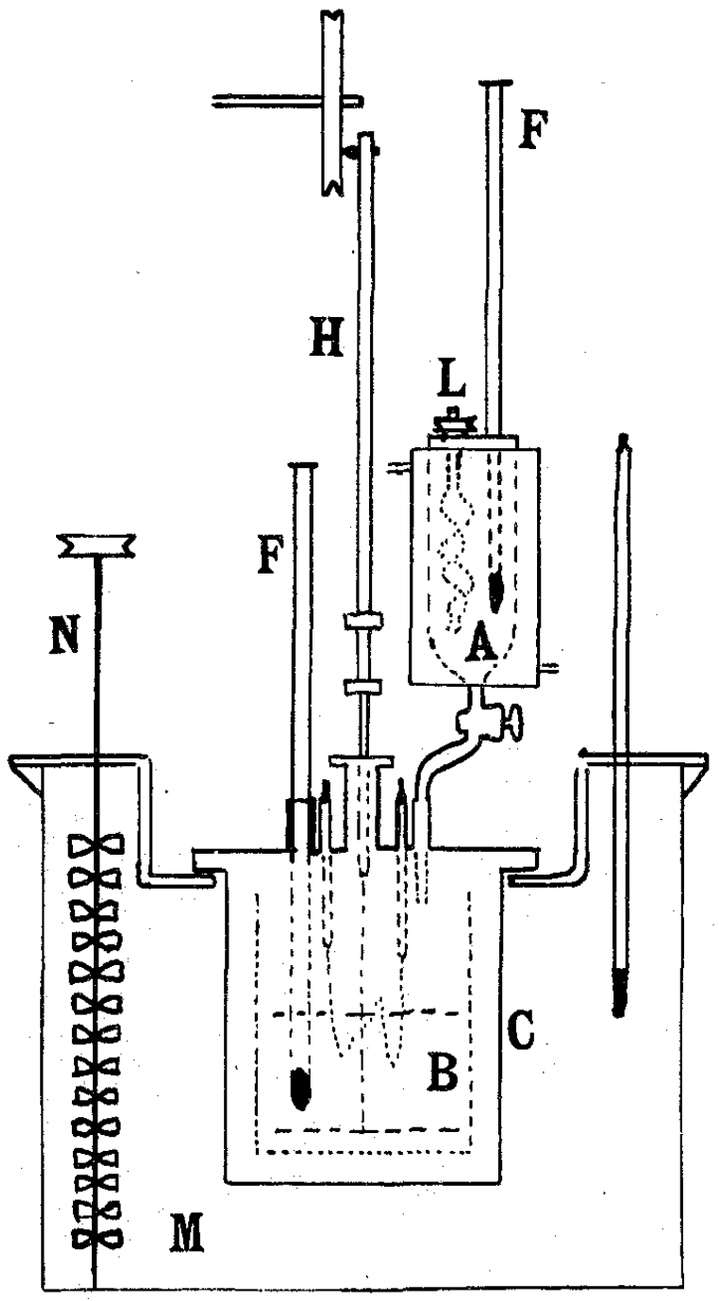


FIG. 1

advantages which are indicated in their paper. It consists in the measurement of the temperature rise produced in the complete system (of calorimeter, neutralised solution, stirrer, etc.) by the supply of a known quantity of electrical energy to a heating coil immersed in the calorimeter liquid. In the application of the method, two problems arise, namely the construction of a coil immersible in alcoholic solutions of acid and alkali and the accurate and convenient measurement of the electrical energy supplied to it.

[1] J. Am. Chem. Soc., **39**, 2110 (1917).

The crux of the first problem lies in the selection of an insulating covering. Previous workers, dealing with aqueous solutions, have used such coatings as shellac or asbestos inside a copper tube, which are inapplicable to the present work. Richards and Daniels[1] used a glass capillary as casing for the coil in their work on thallium amalgams but it was found difficult to repeat their method of preparation. An alternative method was developed which pro-

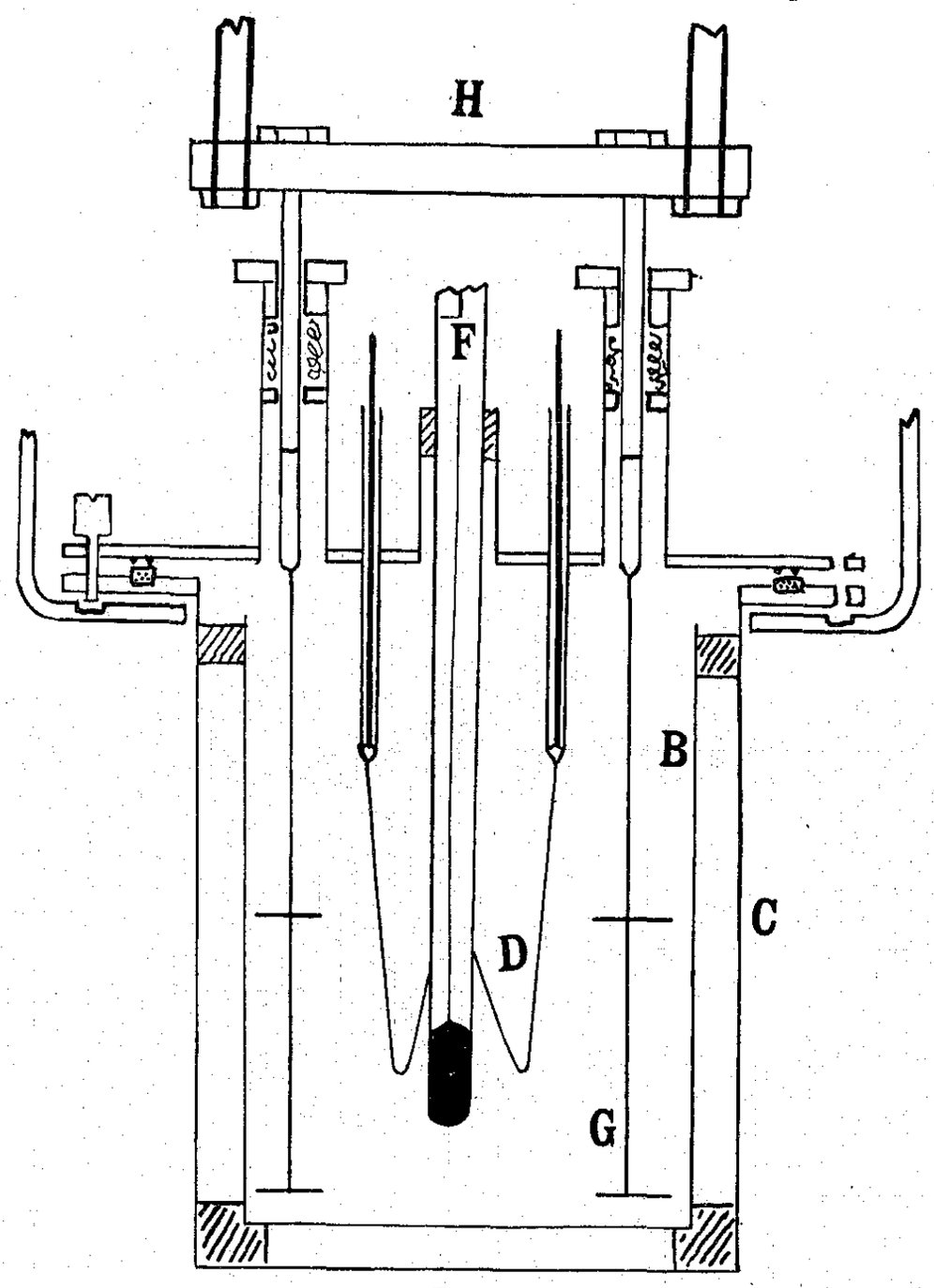


FIG. 2

duced a glass-cased manganin coil which we employed as the electrical calorifer. A length of manganin wire (S.W.G. 30) is pushed through a piece of soft glass capillary tubing and then, after forming a thick collar of very

[1] J. Am. Chem. Soc., **41**, 732 (1919).

hot glass at the middle of the tube, the tube is drawn out rapidly and forms a thin and fairly uniform casing over the wire. After annealing, the wire is bent to the required form. Copper leads are then put in at each end and electrical contact is made by a little Rose's metal; electrical heating enables the melting up and cooling down of the latter to be done sufficiently slowly to prevent the glass from cracking at the shoulder where the join takes place. The coil is fixed in the calorimeter through the chimneys so that the contracted portion containing the manganin wire is well below the surface of the calorimeter liquid.

The problem of the measurement of the electrical energy has received various solutions according to the various combinations of the factors of voltage, time, resistance etc. in terms of which the electrical energy was measured. A simple method, which does not appear to have been used previously in thermochemical calorimetry, was employed in which only two factors, voltage and quantity of electricity are measured. The apparatus is arranged in the following way. The heating current supplied by accumulators is passed through the glass-sheathed calorifer coil, a variable resistance and a copper coulometer in series. A branch circuit from the terminals of the coil contains a sensitive mirror-galvanometer and three standardised cadmium cells in opposition to the potential drop across the heating coil due to the accumulators. By manipulation of the variable resistance, the galvanometer reading is kept at zero and thus the potential drop across the coil is maintained exactly equal to the aggregate E.M.F. of the three cadmium cells. A knowledge of the E.M.F. of the cells and the amount of copper deposited in the coulometer after any given run will then give the amount of electrical energy expended between the terminals of the calorimeter heating coil. The method has the advantages that the amount of energy delivered is referred directly to the two fundamental electrical units, that only one quantity (the mass of the copper deposit) has to be determined after each run and that the technique is so simple that an unskilled assistant has no difficulty in maintaining the potential drop correct to within .02%.

Although longer coils could probably be produced with additional care and practice, it was not found practicable to make coils exceeding 35 cm. in length. This shortness made the end-corrections for leakage along the leads rather large. It could not therefore be assumed that the electrical energy dissipated between the terminals of the heating coil, as measured above, had all been spent in raising the temperature of the calorimeter system. Instead, the heat yield of the calorifer per gramme of copper deposited was determined by measurements made with the calorimeter system of calculated thermal capacity filled with a weighed quantity of water. An added advantage of such a calibration is that it corrects for systematic errors in the electrical measurements. From a number of concordant experiments of this nature it was found that one gramme of copper deposited raised the equivalent of 589 grammes of water through 3.642° (reduced to the hydrogen scale). From this it can be deduced that the heat yield of the calorifer is 2145 calories per gramme of copper deposited, corresponding to 97.0% of the energy dissipated

between the terminals of the heating coil. The limiting error in this determination is probably the one involved in the value of the Beckmann thermometer degree on the hydrogen scale.

We do not consider that the calorifer was completely satisfactory. In all the measurements made with it, there were persistent and apparently random variations within a range of 1% in the temperature rise for a given system per gramme of copper deposited. The responsibility, however, is shared by the Beckmann thermometer and the allocation of the blame. The error involved was minimised by repeating the calorifer measurement several times for each system and taking a mean of the results. The defects of the calorifer are almost certainly connected with the coil itself; the measuring system proved quite satisfactory and very convenient. The use of a longer coil with smaller end-leakages would materially increase the accuracy of the method.

Thermometry. Two Beckmann thermometers, graduated in hundredths of a degree, were used to record the temperature of the liquids in the calorimeter and the alkali vessel. The calorimeter thermometer was fitted with an electromagnetic tapper to eliminate lag in the mercury thread. These two thermometers were compared with one another over the range of temperature at which mixture took place, in a sensitive thermostat with precautions to eliminate lag. The temperature of the alkaline solution could then be expressed in terms of the calorimeter thermometer immersed in the acid solution.

It was further necessary to know the value of the readings of the calorimeter thermometer in terms of the hydrogen scale. For this purpose it was compared with a thermometer standardised by the National Physical Laboratory whose corrections were given to five hundredths of a degree. An auxiliary calibration of the calorimeter thermometer was carried out using the electrical calorifer in the manner described by Richards and Tamaru.[1] The latter calibration afforded no information as to the absolute value of the scale divisions but supplied a useful check on the relative value of the various parts of the calorimeter thermometer scale. All temperature differences were reduced to the hydrogen scale.

The standardisations gave striking evidence of the defects of the Beckmann thermometer as an instrument of precision. It was shown that the bore of a Beckmann may vary by as much as 2% in adjacent degree lengths and in a most irregular manner. Experience with a number of Beckmanns also showed the most tenacious "sticktion" in the majority of cases; in spite of vigorous tapping they will fail to show the constant oscillations in temperature of a thermostat within a range of .01° as recorded on a similar but more reliable instrument.

Materials. The large quantities of pure dry methyl alcohol needed for the work was prepared in the manner described by Hartley and Raikes[2], except that the final distillation from copper sulphite was omitted. The product

[1] J. Am. Chem. Soc., **42**, 1374 (1920).
[2] J. Chem. Soc., **127**, 504 (1925).

usually contained about .025% and never more than .05% of water; no appreciable quantity of either acetone or aldehyde was present.

Hydrogen chloride was prepared by the action of pure sulphuric acid on pure dry sodium chloride. The gas was passed through a glass-wool spray filter and a series of traps into methyl alcohol cooled in ice and salt. The cooling of the alcohol was desirable in view of the large heat of solution of the gas and the high temperature coefficient of esterification.

Hydrogen bromide was prepared by dropping syrupy phosphoric acid on to a mixture of sodium bromide and about twice its bulk of phosphorus pentoxide. The gas was passed through two drying tubes of calcium bromide into cooled methyl alcohol.

Pure glacial acetic acid was freed from the last traces of water by fractional crystallisation, the whole process being carried out without access to any but carefully dried air. The salicylic acid used was a commercial sample with a corrected melting point of 159°.

In the earlier experiments, sodium methylate was prepared by dissolving freshly scraped sodium in methyl alcohol, the operation being performed in a "dry-box" filled with dry nitrogen. Later an improved and simplified method, devised by Mr. W. F. K. Wynne-Jones in this laboratory, was employed. Pure sodium was melted in a small Pyrex flask under heavy paraffin and was strained by being drawn up by suction into clean glass tubes, whence it was discharged into another flask under fresh paraffin. The strained sodium was again melted and drawn into glass tubes where it was allowed to solidify. The length of tubing containing the requisite amount of sodium was then cut into short lengths and dropped into the alcohol. The sodium dissolved slowly and was prevented from rising to the surface by its glass casing.

Ammonia was prepared by gently heating a mixture of ammonium chloride with powdered lime. It was passed into methyl alcohol after drying with solid caustic soda and lime. Aniline was dried over calcium chloride and fractionated through a short three-bulb column.

The solutions of the organic acids and of aniline were made up by weight. The solutions of hydrogen chloride, hydrogen bromide, sodium methylate and ammonia were estimated volumetrically by weight titration against decinormal hydrochloric acid or caustic soda containing baryta, using methyl red as an indicator, which gave sharp end-points.

It was discovered at the outset of the work that solutions of hydrogen chloride in methyl alcohol esterify with appreciable velocity. A few rough measurements of the velocity of esterification, expressed as percentage change per day, are given:—

Solutions of hydrogen chloride at 16° and various concentrations

Weight Normality	0.1	0.4	2.0
Rate per day	.03%	.12%	.60%

0.27 weight-normal solution of hydrogen chloride at various temperatures

Temperature	8°	17°	25°
Rate per day	.04%	.14%	.70%

These approximate results show the substantial value of the change which has sometimes been neglected. These and similar experiments with hydrogen bromide solution bring out the facts that the rate of change is roughly proportional to the concentration of the solution, is very sensitive to temperature and is much bigger for hydrogen bromide than for hydrogen chloride. In view of this the solutions of the two acids were always cooled in ice and salt during preparation and were afterwards kept in a cellar at about 8°. They were also always standardised after, as well as before a series of experiments.

The Possible Sources of Error and their Relative Significance

Errors in thermometry. The accuracy attainable with the Beckmann thermometers used has already been discussed. The irregularity of the stem, the possibilities of lag and the reduction of temperature differences to the hydrogen scale might each contribute an uncertainty of .005° to the temperature readings.

Errors in the measurement of electrical energy supplied to the calorifer. There are two possibilities of error, namely in the measurement of the potential drop across the coil and in that of the quantity of electricity passed. As indicated earlier the P.D. was readily maintained within .02% of the correct value. In the quantity measurements two coulometer were used in series and their deposits agreed to within .5%. Any systematic error in the deposition was corrected for by the water calibration of the calorifer.

Errors in the thermal efficiency of the calorifer. The water calibration of the calorifer made it possible to evaluate the heat yield per unit quantity of electricity with satisfactory precision. From the successive calorifer runs with known masses of methyl alcohol (or solutions of substantially the same specific heat) carried out after neutralisation experiments, it was shown that the efficiency had undergone no secular change in value during the course of the work.

Errors due to loss or gain of heat by the alkaline solution during its transfer to the calorimeter. Blank experiments were carried out with methyl alcohol substituted for both the acid and alkaline solutions of the neutralisation experiments. The temperature of the room was sometimes adjusted so as to be substantially higher than the temperature of mixing but the result of the experiments was very satisfactory and indicated that the temperature change during mixing was not likely to exceed .004° in the mixed liquids under even the least favourable conditions.

Errors due to failure to maintain the adiabatic condition. The most obvious way in which such an error could arise was by lack of control of the temperature of the paraffin bath but it was shown that the heating and cooling coils were entirely satisfactory in this respect. The heating coil had a lag of only five or ten seconds; that for the cooling coil was about twice as long. It was found to be a matter of no difficulty to keep the bath within .02° or .03° of the temperature of the calorimeter except for a short initial period of a few seconds during the very rapid temperature rises which follow the mixing of

the most concentrated solutions. Small variations of this order, random in algebraic sign, can be dismissed as negligible.

A less obvious uncertainty is a much more important source of error. At what temperature should the jacketing bath be maintained? Temperature equality between calorimeter and jacket will not necessarily preserve constancy of temperature of the calorimeter liquid because heat is being generated by the stirrer and heat is being lost by evaporation from the calorimeter. Only when these two opposing factors exactly balance each other will the adiabatic condition be maintained. In general, there will be a certain temperature difference or "thermal head" between jacket and calorimeter corresponding to constancy of calorimeter temperature; this we may call the adiabatic thermal head. This quantity will depend in magnitude and sign—let us adopt the convention that the thermal head is positive when the jacket is warmer than the calorimeter—on the nature of the stirring and the volatility of the calorimeter liquid.

Numerous experiments were carried out to examine this point. They took the form of measurements of the leakage coefficient (i.e., the rate of change of calorimeter temperature per unit thermal head) with different liquids and varying thermal heads. With nitrobenzene, as one would expect with a non-volatile liquid, the adiabatic thermal head was negative and about $-.11°$. Furthermore in the absence of the erratic evaporation factor, the proportionality of leakage to thermal head was strictly maintained. With water, the adiabatic thermal head was nearly zero; that is to say temperature equality of jacket and bath corresponded to constant calorimeter temperature. As Barry[1] has shown however, leakage across the air-gap of an open calorimeter containing water is quite a complex phenomenon and varies with the state of the air-gap, whether it be wet or dry.

It was therefore to be expected that with a liquid as volatile as methyl alcohol, the evaporation factor would become more important and complicated. Such was found to be the case. It was impossible to fix any reproducible value for the adiabatic thermal head. Determinations at various times led to values lying in a random manner between $+.15°$ and $+.50°$. The erratic nature of the values must depend on the volatility of methyl alcohol, the state of the air-gap and the possibility, when the methyl alcohol has been enclosed in the calorimeter for some time, of evaporation from the sides of the calorimeter back to the submarine. Whatever the factors involved are, it is clear that the heat-transfer across the air-gap is not a simple function of the thermal head. The uncertainty which this occasioned in the maintenance of the adiabatic condition, was minimised by taking an average value for the adiabatic thermal head of $+.25°$ and modifying this value when the readings of the calorimeter temperature before mixing seemed to indicate that the state of the air-gap corresponded to a different value.

The error which this uncertainty might involve depends on the magnitude of the thermal leakage when the jacket temperature was not properly ad-

[1] J. Am. Chem. Soc., **44**, 899 (1922).

justed. It was found that with the jacket .1° greater or less than the correct temperature, heat transfer took place at the rate of .25 calories per minute[1]. The maximum error likely to occur in a ten minute run (while about 800 calories are being generated in the calorimeter) may therefore be estimated as about 2.5 calories or .3% of the quantity being measured.

Results

The following heats of neutralisation refer to 17°C. and are expressed in calories per mole; the concentrations are expressed in moles per thousand grammes of solution.

Sodium methylate and hydrogen chloride

Weight				
Normality	0.247	0.1040	0.1010	0.0530
	12,160	11,840	11,760	(11,520)
	11,970	11,780	11,760	11,520
	11,850	11,810	11,660	(11,320)
	11,970	(11,410)	11,900	11,600
	(11,420)			11,750
				11,420
Mean values adopted	11,920	11,770	11,770	11,550

The bracketed values were given half weight because there was independent reason to suspect their accuracy.

Sodium methylate and hydrogen bromide

Weight				
Normality	0.234	0.0979	0.1015	0.0470
	11,570	11,580	11,370	11,470
	11,750	11,300	11,340	11,230
	11,660	11,580	11,390	11,410
	11,700	11,240	11,400	11,130
	11,560			11,250
Mean values adopted	11,650	11,430	11,380	11,280

Sodium methylate and acetic acid

Weight			
Normality	0.248	0.0980	0.0473
	6,820	6,780	6.710
	6,740	6,770	6,740
	6,800	6,720	6,640
	6,790	6,780	6,700
Mean values		6,800	6,790
adopted	6,790	6,750	6,720

[1] It is interesting to note that the theoretical conductivity of an air-gap of the dimensions used, calculated from Barry's empirical formula (J. Am. Chem. Soc., **44**, 929 (1922)), would cause a heat transfer of .14 calories per minute with .1° thermal head.

Sodium methylate and salicylic acid

Weight		
Normality	0.253	0.0981
	6,100	6,100
	6,160	6,055
	6,075	5,960
	6,045	5,980
Mean values adopted	6,100	6,020

Ammonia and hydrogen chloride

Weight			
Normality	0.222	0.093	0.0468
	17,710	17,290	17,290
	17,910	17,860	17,360
	17,840	17,600	17,730
	17,700	17,600	17,810
	17,830	17,630	17,700
Mean values adopted	17,800	17,630	17,630

Aniline and hydrogen chloride

Weight			
Normality	0.367	0.205	0.0987
	10,740	10,200	10,040
	10,790	10,200	9,960
	10,790	10,170	9,875
	10,750	10,190	9,845
Mean values adopted	10,770	10,190	9,930

Specific heat of methyl alcohol

From the calorifer runs in methyl alcohol, carried out to test the calorifer as well as those performed in the diluter solutions, it was possible to calculate the specific heat of methyl alcohol. This leads to a value of 0.632 which is rather higher than most of the previous determinations; (Regnault 0.601, Bose 0.607, Kopp 0.645, Lecher 0.624, Timofejew 0.600).

Discussion

The results fall into three categories: heats of neutralisation of strong acids by strong bases, of weak acids by strong bases and of strong acids by weak bases.

The heats of neutralisation of hydrogen chloride and hydrogen bromide by sodium methylate show a diminished magnitude with increasing dilution

similar to that observed in aqueous solution by Richards and Rowe[1]. The rate of fall in value with dilution is substantially greater than in aqueous solution; however it is to be observed that, although the concentrations employed were in every case lower than those of Richards and Rowe, the ratio of Λ_c to Λ_o for the electrolytes was smaller. Thus the ratio of Λ_c to Λ_o for twentieth-normal hydrogen chloride in methyl alcohol is about 0.68 and the values for sodium methylate and sodium chloride are of the same order; on the other hand the most dilute solution of Richards and Rowe have a ratio of Λ_c to Λ_o of about 0.90. The approximate nature of the measurements makes no precise extrapolation worth consideration but the trend of the values for hydrogen chloride and hydrogen bromide points to a limiting value of about 11,200 calories at infinite dilution. This approximate value of the heat of ionisation of methyl alcohol may be compared with the value for water and with the value of 11,200 calories obtained by Deventer and Reicher[2] for the heat of neutralisation of sodium ethylate by hydrogen chloride in ethyl alcohol. The latter value has to be corrected for the heat of precipitation of sodium chloride, estimated by Tanatar and Klimenko[3] to be 362 calories, but it is clear that the heat of ionisation of ethyl alcohol is very similar to the value for methyl alcohol.

In the case of the results for acetic and salicylic acids, by subtracting the values from the heat of neutralisation of the strong acids we may calculate the heat of ionisation of salicylic and acetic acids. Thus adopting 11,200 calories for the limiting value for strong acids and taking 6,750 calories and 6,020 calories for the heats of neutralisation of acetic and salicylic acids respectively in decinormal solution, we may infer that the heats of ionisation of acetic and salicylic acids are respectively $-4,450$ calories and $-5,180$ calories. The similarly determined quantities for aqueous solution are -400 calories and $-1,320$ calories. Thus in both cases much more heat is absorbed when the acid ionises in methyl alcohol but the difference between the two acids is of the same order in both electrolytes. If the heat of ionisation is regarded as the sum of a negative heat of ionisation of the acid molecule and the positive heat of solvation of the resultant ions, we may account for the larger negative values in methyl alcohol by the smaller affinity of the ions for the alcoholic solvent. The strong depressive effect of traces of water on the mobility of hydrion in methyl alcohol and on its catalytic activity is evidence for such a marked difference in affinity.

The values for the heat of neutralisation of ammonia and aniline by hydrogen chloride are particularly interesting. Comparing them with the corresponding values for aqueous solution and with the value of Tanatar and Pissarzewsky[4] for ammonia in ethyl alcohol we have:

[1] J. Am. Chem. Soc., **44**, 684 (1922).
[2] Z. physik. Chem., **8**, 536 (1891).
[3] Z. physik. Chem., **27**, 172 (1898).
[4] Z. physik. Chem. **25**, 379 (1898).

Heats of neutralisation by hydrogen chloride, in calories.

	in water	in methyl alcohol	in ethyl alcohol
Ammonia	12,300	17,630	17,854
Aniline	7,500	9,930	———

These results draw attention to the peculiar nature of the neutralisation of bases like ammonia and aniline by acids. It still seems customary to consider the value of 12,300 calories for the neutralisation of ammonia by acids in aqueous solution as evidence for the weakness of the base and to regard the residual 1,400 calories simply as the heat absorbed in the ionisation of the ammonia[1]. It has been pointed out often, however, that to regard an aqueous solution of ammonia as containing nothing but ammonium hydroxide and a small number of ammonium ions is wrong. It is much more probable that a considerable fraction of the solute is present as free unhydrated ammonia.[2]

In the absence of positive evidence of the existence of ammonium methylate and anilinium methylate in the methyl alcohol solutions of the respective bases, it seems more reasonable to regard the respective values of 17,630 calories and 9,900 calories as approximations to the heat change accompanying the two reactions:

$$NH_3 + H^{\cdot} = NH_4^{\cdot}$$
$$C_6H_5.NH_2 + H^{\cdot} = C_6H_5.NH_3^{\cdot}$$

On this hypothesis the larger heats of neutralisation in methyl alcohol may be connected with the fact that the hydrion has a smaller affinity for methyl alcohol than for water.

Summary

(1) The heats of neutralisation of hydrogen chloride, hydrogen bromide, acetic and salicylic acids by sodium methylate and of aniline and ammonia by hydrogen chloride have been measured in methyl alcohol solution over a range of concentration in an adiabatic calorimeter.

(2) The heat of formation of methyl alcohol from its ions is 11,200 calories.

(3) The heats of ionisation of acetic and salicylic acids in methyl alcohol are −4,450 calories and −5,180 calories respectively.

(4) The heats of formation of ammonium and anilinium ions from free base and hydrion in methyl alcohol are 17,630 calories and 9,900 calories respectively.

Physical Chemistry Laboratory,
Balliol College and Trinity College,
Oxford.
January 19, 1927.

[1] See, for example, Nernst: "Theoretische Chemie," 683 (1921).

[2] Moore: J. Chem. Soc., **91**, 1379 (1907); Scheffer and Wijs: Rec. Trav. chim., **44**, 655 (1925).

2-170

CATALYTIC ACTIVITY OF LEAD

BY F. A. MADENWALD, C. O. HENKE AND O. W. BROWN

Introduction

Finely divided lead prepared from commercial oxides was previously used as catalyst[1], and it has been shown to be excellent for the hydrogenation of nitrobenzene. It produces not only aniline, but is also one of the three catalysts that produces azobenzene in considerable amounts. In this paper results are given of an extensive study of the behavior of lead catalysts made from carefully purified materials.

Experimental Details

The apparatus and general proceedure used in this work were the same as those described in an earlier paper[2], with slight modifications as noted in Jour. Phys. Chem., **26**, 324 (1922).

In each experiment 2 cc. of nitrobenzene (2.322 g.) was used, its rate of flow being 4 g. per hour. The rate of flow of hydrogen was 14 liters per hour, giving an excess of 540% of the amount necessary to reduce the nitrobenzene.

Preparation of the Catalysts

The lead nitrate used in the preparation of the catalysts contained the following impurities: insoluble substances 0.009%, copper 0.0025%, iron 0.001%, and earths and alkalis 0.1%. This product was dissolved in hot water, filtered, and allowed to crystallize. The crystals were filtered on a Buechner funnel, washed, and then dried by drawing air through them. The lead prepared in this way was the material from which all catalysts were prepared.

Lead carbonate was prepared by adding a solution of 600 g. of sodium carbonate in 4700 cc. water to a solution of the recrystallized lead nitrate containing 2,000 g. in 5,000 cc. of water. The sodium carbonate was made by heating Baker's C. P. sodium bicarbonate for several hours at 180°C. The precipitated lead carbonate was washed well with distilled water by decantation, to remove soluble salts. It was then filtered on a Buechner funnel and further washed three times with distilled water. The lead carbonate was dried in a vacuum drier and then ground and passed through a 60 mesh sieve.

All but 50 g. of the carbonate was converted to red lead by roasting it for $10\frac{3}{4}$ hours at 430°C. in an electric muffle. The apparent density of the resulting red lead was determined by means of Dr. Schaeffer's modification[3] of the Scott Volumeter and found to be 11.7 g. per cu. in. An analysis of the red lead showed that it contained 33.1% lead peroxide.

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[1] Henke and Brown: J. Phys. Chem., **26**, 324 (1922).

[2] Brown and Henke: J. Phys. Chem., **26**, 161, 631 (1922).

[3] Schaeffer, White, and Calbeck: "Chemical Analysis of Lead and Its Compounds", p. 148 (1922).

A second red lead was made by roasting 600 g. of the recrystallized lead nitrate. The nitrate was put in a covered dish and then placed in a muffle. During the first two hours of heating, the dish was kept covered but when the sputtering, due to the decomposition of the lead nitrate had ceased, the cover was removed. After 10 hours roasting at 430°C. the material was passed through a 60 mesh sieve. Then it was heated, with frequent stirring, for 30¾ hours more at 430°C. The apparent density of this red lead was 23.3 g. per cu. in.

Litharge was then made, one from each of the above red leads, and these were put into the electric muffle and heated to a temperature of 550°C. and 600°C., a current of air passing over them. The red lead prepared from the carbonate was heated for 10 hours at 550°C., and for 12 hours at 600°C., giving the product a peculiar brown color. It contained 2% lead peroxide and its apparent density was 16.5 g. per cu. in. The red lead from the nitrate was heated for 18 hours at 550°C. and for 12 hours at 600°C. The color of the product was black; it contained only 8% of peroxide, and had an apparent density of 25.4 g. per cu. in.

Experimental Results

The activity of the lead catalysts made from the carbonate, the light red lead (11.7 g. per cu. in.), the heavy red lead (23.3 g. per cu. in.), the heavy litharge (25.4 g. per cu. in.), and the light litharge (16.5 g. per cu. in.) was studied. The same amounts of each catalyst by volume were put into a catalytic furnace and treated alike. They were each reduced for one hour at 308°C. with the rate of flow of hydrogen at 14 liters per hour. Nitrobenzene and hydrogen were then introduced.

It was found that these lead catalysts act the same as copper catalysts, concerning the increase in activity with use. However, in the case of lead catalysts the increase is slower, requiring 60 to 70 experiments to obtain a constant yield; in the case of copper 6 to 8 experiments were sufficient. There were usually 8 experiments carried out each day. On the first day the activity of the catalysts was poor. The yields of aniline and azobenzene with the different catalysts were as follows: catalyst from light red lead (11.7 g. per cu. in.) 10.2% aniline, no azobenzene; heavy red lead (23.3 g. per cu. in.) aniline 45.7%, azobenzene 14%; heavy litharge (25.4 g. per cu. in.) aniline 41.4%, azobenzene 11.05%; light litharge (16.5 g. per cu. in.) aniline 73.4%, azobenzene 12%; and lead carbonate, aniline 29.1%, azobenzene 9%.

Upon use the activity of the catalysts gradually increased until they reached a constant yield of 95% to 96% of aniline on the eighth day. However, the azobenzene yield decreased with use of the catalyst, none being produced at the end of the third day.

The catalyst from light litharge (16.5 g. per cu. in.) which gave the highest yield on the first day's run, seems to be the best. After using it in nearly 200 experiments sometimes at a temperature 16°C. above the melting point of lead, it was still a loose mass of black powder containing no pellets of massive lead.

The effect of temperature on the activity of this catalyst was studied. Each result is the average of about eight experiments performed. The results are given in Table I.

TABLE I

Rate of flow of hydrogen—14 liters per hour.
Rate of flow of nitrobenzene—4 g. per hour.
Excess of hydrogen—450%.

Temperature	Per cent aniline	Per cent azobenzene	Total
290 C.	82.5	2.3	84.8
212	70.7	11.5	82.2
255	30.0	——	30.0
308	97.1	——	97.1
327	95.5	——	95.5
346	92.6	——	92.6
308	96.6	——	96.6

From the results given in Table I it seems that the best temperature for the production of aniline is 308°C. Experiments were carried out to compare the efficiency of the catalysts used in a glass tube with those used in an iron tube. The light litharge (16.5 g. per cu. in.) was again used in making this

TABLE II

Catalyst—Light litharge (16.5 g. per cu. in.).
Rate of flow of hydrogen—14 liters per hour.
Rate of flow of nitrobenzene—4 g. per hour.
Temperature—308°C.
Excess of hydrogen—450%.

Unground material compressed 29 grams			Material ground 54 hrs. 33.3 grams			Material ground 108 hrs. 35.1 grams			Material ground 200 hrs. 40.0 grams		
Aniline	Azobenzene	Total	Aniline	Azobenzene	Total	Aniline	Azobenzene	Total	Aniline	Azobenzene	Total
Daily average, material yield in per cent theory.											
22.4	6.6	29.0	28.1	14.4	42.5	55.1	30.0	85.1	36.0	23.1	59.1
39.8	16.0	55.8	60.7	23.0	83.7	81.8	10.3	92.1	76.5	8.1	84.6
64.2	25.3	89.5	77.7	13.0	90.7	45.6	0.6	46.2	87.0	——	87.0
93.6	——	93.6	90.2	——	90.2	67.8	12.6	80.4	90.4	——	90.4
95.5	——	95.5	94.2	——	94.2	85.2	——	85.2	92.9	——	92.9
95.8	——	95.8	96.2	——	96.2	92.4	——	92.4	94.7	——	94.7
96.1	——	96.1	——	——	——	95.9	——	95.9	75.7	——	75.7
——	——	——	——	——	——	——	——	——	96.3	——	96.3
——	——	——	——	——	——	——	——	——	97.6	——	97.6

comparison, and it was found that it became active sooner when put in an iron tube than when put in a glass tube. Ninety-seven percent yield of aniline was secured on the fifth day, using an iron tube. When a glass tube was used a 93.5% yield was obtained on the fifth day, and a 96.5% yield on the eighth day.

A study was undertaken to determine what the effect of grinding would be upon the activity of the catalyst. A quantity of red lead (11.7 per cu. in.) was ground in a ball mill. Samples were taken from the mill after 54, 108, and 200 hours of grinding. The apparent density of these red lead samples was 17.4, 21.7, and 30 g. per cu. in., respectively. In order to aid the grinding somewhat, the red lead was loosened from the sides of the ball mill every 12 hours. The data are given in Table II.

Although the catalyst from the ground material gave low yields on the first day, they were higher than those obtained from the unground material. But similar to the unground catalysts, the activity increases with use. The effect of grinding, however, was only important to the extent of increasing the apparent density of the catalyst so that more could be packed in the catalyst tube.

The catalyst made from the material ground 108 hours was on the third day's run heated for a short time by mistake to 443°C., which is 116 degrees above the melting point of massive lead. This overheating killed its activity, giving on the next day's run only an average of 45.6% yield of aniline, as compared with the previous average yield of 81.8%. However, this loss in activity was only temporary, and on the seventh day the yield reached 95.9% of aniline. This behavior of lead catalysts after heating to a high temperature in hydrogen is different from that of copper and nickel catalysts.[1]

In continuing the study of the increase in activity with use, two catalysts were prepared from the material ground 108 hours. They were both reduced for one hour at 308°C. Hydrogen was passed over one of them at this temperature for 48 hours, which time was equivalent to four days use. The following day seven experiments were carried out with this catalyst, the average yield being 4.4% aniline and no azobenzene. This shows that hydrogen alone kills the activity of the catalyst as it causes its physical condition to be changed. It becomes agglomerated into pellets of massive lead of various sizes, with only slight traces of active, loose catalyst.

Through the other catalyst from the same material, 80 cc. of nitrobenzene was passed at the rate of 4 g. per hour. It was passed continuously stopping only at night, each day corresponding to a five day run with the other catalyst. The object in view was to determine whether or not this would cause the same increase in activity of the catalyst as when used in 2 cc. portions, with intervals of 30 minutes required to remove the products from the furnace. After feeding 80 cc. of nitrobenzene continuously, experiments were made as in Table II. The average yield on the first day was 94.6% aniline, with no azobenzene, and on the second day 94.7% aniline, with no azobenzene.

[1] Brown and Henke: J. Phys. Chem., **26**, 161-190 (1922).

These two days would correspond to the sixth and seventh days use, as figured from the amount of nitrobenzene passed over the catalyst. Comparing these yields with those obtained when used intermittently, (Table II catalyst ground 108 hours) it will be seen that on the seventh day 95.9% yields of aniline were secured, while they were only 94.7% in this case. This indicates that there was practically no difference between the intermittent and continuous use of a catalyst at 308°C. for bringing it up to its maximum activity. Hydrogen alone kills the activity.

The yield of azobenzene were obtained with both the ground and unground catalyst only on the first few days as has been shown, the highest yield being 25.3%. Lead, bismuth, and thallium are the only catalysts that give high yields of azobenzene.[1] Copper and nickel, although in many cases are very active catalysts, gave no azobenzene. The factors which determine whether or not a catalyst may give azobenzene are: first, the metal which constitutes the catalyst; second, the activity of the particular catalyst; and third, the temperature. All the previous experiments were carried out with the rate of flow of hydrogen 14 liters per hour and the rate of flow of nitrobenzene 4 g. per hour. Experiments were also made with different rates of flow of both hydrogen and nitrobenzene at the same temperature of 308°C.. The catalysts used were light red lead (11.7 g. per cu. in.) and light litharge (16.5 g. per cu. in.). The yields at different rates varied from 65% to 97% of aniline, the two catalysts giving about the same yields at different rates. The best results were obtained with the rate of 14 liters of hydrogen and 4 g. of nitrobenzene per hour, while both higher and lower rates gave poorer results.

Conclusion

1. Lead catalysts prepared by different methods were compared.
2. The activity of lead catalysts increases slowly with use.
3. Different lead catalysts showed greater difference in activity on the first day's run, but by the eighth day their activities were practically the same.
4. A catalyst made from heavy litharge was used for nearly 200 experiments, maintaining about 97% yield of aniline.
5. Hydrogen alone kills the activity of the catalyst.
6. Activity of the catalyst increases more rapidly in an iron tube than in a glass tube.
7. Lead catalyst works best for the reduction of nitrobenzene at 308°C.
8. The grinding of the material in order to increase its apparent density had no permanent effect on the activity of the catalyst produced.
9. The activity of the catalyst was only temporarily destroyed by heating it at 450°C. in hydrogen.

Laboratory of Physical Chemistry,
Indiana University, Indiana.

[1] Henke and Brown: J. Phys. Chem., **26**, 324 (1922).

INFLUENCE OF HEAT AND HYDROGEN ION CONCENTRATION ON BIOLOGICAL TRANSPORTATION SYSTEMS CONTAINING SULFUR[1].

BY F. F. NORD[2]

Proceeding from considerations of Hottinger[3] the suggestion was put forward recently[4] that an intermediate systems with undetermined structure serves as nucleus of those highly reactive oxygen addition compounds formed by cysteine and reduced gluthatione, which were supposed to have a decisive role in reversible physiological processes.

The latter addition-compounds probably represent new members of that group of systems which—as we know also from certain processes concerning the cell—might be regarded as the "transportation form"[5] in contradistinction to the usual structural forms of biologically active substances.

Since the work reported in this paper was completed it has been indicated[6] that the chief characteristic of the transportation form of a compound or system may be regarded as its capability either to mediate in intermittent actions, or to enable irreversible reactions to proceed, especially in cases where the use of a potentially higher energy content is involved. It is not supposed to exist in a form which can be investigated successfully by means of our present tools as a chemical entity. Since its capacity to promote the aforementioned types of biological reactions is probably due in the main to an electron transfer caused by the ionic antagonism within the cell, it is probable that model experiments on analogous systems will not at present authorize us to do more than intimate their manner of functioning. Ionic antagonism, we know, also exerts a great influence upon enzyme action, and there are certain reasons for assuming that the same is also true for the influence of adsorption.

However, lacking convenient terms for its demonstration, it seems to be difficult, even in biochemical relations, to abandon the structural conceptions at present and to adopt on a larger scale a much-needed and much more flexible visualization, such as that conveyed by the term "transportation form".

Besides the aforementioned sulfur systems which again might differ in the model experiment and the cell, only a few examples of transportation forms are supposed to exist (e.g. certain compounds of the bile promoting the

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[1] Work carried out in 1926 in the Section of Biochemistry, the Mayo Foundation, Rochester, Minn.

[2] Present address: Division of Agricultural Biochemistry, University of Minnesota, St. Paul, Minnesota.

[3] A. Hottinger: Schweizerische medizin. Wochenschrift, **53**, 430 (1923).

[4] Edward C. Kendall and F. F. Nord: J. Biol. Chem., **69**, 315 (1926).

[5] F. F. Nord: Chem. Rev., **3**, 49 (1926).

[6] F. F. Nord: Science, **65**, (1927) (in press).

hydro-diffusion of the cell, the enol forms of pyruvic acid, and γ-glucose) which we already know differ in their thermostability or the conditions of the pH necessary for their existence.

Since the unit of the protoplasma is the cell which is surrounded by a colloid cell membrane, it is capable of exerting a great influence through the latter in the regulation for instance, of the permeability[1], the pH and oxidation-reduction potentials. The ionic antagonism in the cell is doubtless influencing the arrangement of the electrons within the system and simultaneously that of the transportation form of a compound. Especially since heat dissociates the complex of adsorption within the living cell[2], it was considered advisable to investigate by means of model experiments the influence of changes in energy condition upon the latter compounds, these changes in energy condition being effected by heat or different pH.

It is recalled in this connection that the existence of the enol forms of pyruvic acid is strongly dependent on the hydrogen ion concentration and these forms again are responsible for its fermentability. The conditions concerning the range of pH are in this case similar to the reversible reaction between tissue, glutathione and hydrogen acceptor[3], in which on the other hand the GSH is supposed to be a thermostable part of the system.

These facts warranted especially the submission of the newly-described, reversible addition systems to the effect of changes in heat, all the more as the chemical nature of these biologically important transportation systems is unknown, and their splitting, following slight changes in the solution, indicates that they cannot be isolated and studied as chemical entities. Some of the early results with solutions containing this type of system showed that, simply on standing, the solution lost its ability to act as an oxidizing agent. This has to be interpreted as a splitting of the essential oxygen addition-product between hydrogen peroxide and cysteine. This work has established the fact that the oxygen addition-product is unstable to heat.

Although it can be formed readily at pH 7.4 it is not essential to have as high a concentration of hydroxyl ion and it is possible to demonstrate the activity of the system at much higher hydrogen ion concentrations.

After it had been shown that cystine and oxidized gluthatione are readily acted upon by suitable reducing agents in the presence of a type of an oxygen transportation system, and since the characteristic of living chemistry is its mutability, it seemed possible that also in the reciprocal effect of the fixed –SH and the –SS groups these or similar transportation forms may be regarded as essential also in promoting the irreversible phase of the reaction.

In the absence of the hydrogen peroxide the formation of this hypothetical system could have been represented by some kind of double-linkage type of combination. Since a molecule in the free state exists in a more condensed phase than the one suitable for a reaction, it is necessary to supply energy to

[1] F. F. Nord: Protoplasma, **2**, No. 2 (1927) (in press).

[2] A. de Gregorio Rocasolano: Rev. de la Academia de Sciencas de Zaragoza, **2**, 92, (1917).

[3] Data concerning systems, where the trimethylamine oxide of Suwa (Arch. ges. Physiol., **129**, 231 (1909)) has the role of the hydrogen acceptor, are not yet available.

the molecule to produce the phase change. This form therefore could have been still more readily explained on the basis of intermediate changes due to the intermittent attachment of an electronegative element. It has been impossible to prepare muscle or boiled yeast suspensions in a manner which does now show a slight reduction of methylene blue in the presence of glutathione. On the other hand no noticeable reduction of indigo carmine could be observed. Since the presence or absence of air produced only very little effect, there is no conclusive indication in these experiments that the same transportation system was present in these cases in a concentration which could be measured by this method.

The present paper contains evidence concerning the energy properties of the reversible system of cysteine and cystine and the destruction of the transportation form in the solution by heat.

Experimental Part

1

The apparatus used for this work was based on the principles of that designed by Clark and Cohen[1] and represented chiefly a multiplication of their single unit. However, the flow of the oxygen-free nitrogen was conducted through a copper tube and greatly facilitated the necessary mobility of the electrode chambers. Two movable burettes, made the addition of different solutions very convenient.

The hydrogen peroxide was diluted to the desired strength from three per cent commercial hydrogen peroxide. Phosphate buffer solutions were used for a pH of 7.4, and the volume was always 100 cc. For the other hydrogen ion concentrations the buffers used are given under the individual experiments. The electrode chambers were heated to 100° by placing in an oil bath which was raised to the desired temperature by an electric heating element. It was found that when the electrode chamber was so heated it could be immediately replaced in the oil thermostat without danger of cracking.

Each of the eight solutions which were used to determine the influence of heat was prepared as follows: 100 cc of phosphate buffer pH 7.4 and 6 cc. of 0.1 N sodium hydroxide were placed in each of the electrode chambers and deoxygenated for one hour with oxygen-free nitrogen. 1.536 g. of cysteine[2] hydrochloride was dissolved in 96 cc. of water. This concentration was equivalent to a 0.1 N solution if the cysteine were pure. As it was only ninety per cent cysteine and ten per cent cystine, the actual concentration of cysteine was 0.09 N. This solution was deoxygenated for one hour and was then added to the phosphate buffer in the electrode chambers. The 6 cc. of sodium hydroxide neutralized all but 6 cc. of the hydrochloride of cysteine and the resulting hydrogen ion concentration of the solution was very near 7.4. Hydrogen peroxide, 0.1 N, and indigo carmine, 0.02 N, were deoxygenated in separate

[1] W. M. Clark and B. Cohen: Public Health Reports, No. 834 (1923); see also Edward C. Kendall and F. F. Nord: l. c.

[2] Compare: S. Sakuma: Biochem. Z., **142**, 68 (1923), or W. F. Hoffman and R. A. Gortner: J. Am. Chem. Soc., **44**, 350 (1922).

burettes. Ten cc. of indigo carmine was added to each electrode chamber. This produced a drop in potential and the indigo carmine remained in the oxidized form; after about forty-five minutes the stream of nitrogen was stopped and the following amounts of 0.1 N hydrogen peroxide were added to the electrode chambers: 1, 1 cc.; 2, 2 cc.; 3, 3 cc.; 4, 4 cc.; 5, 6, 7 and 8, 3 cc. each.

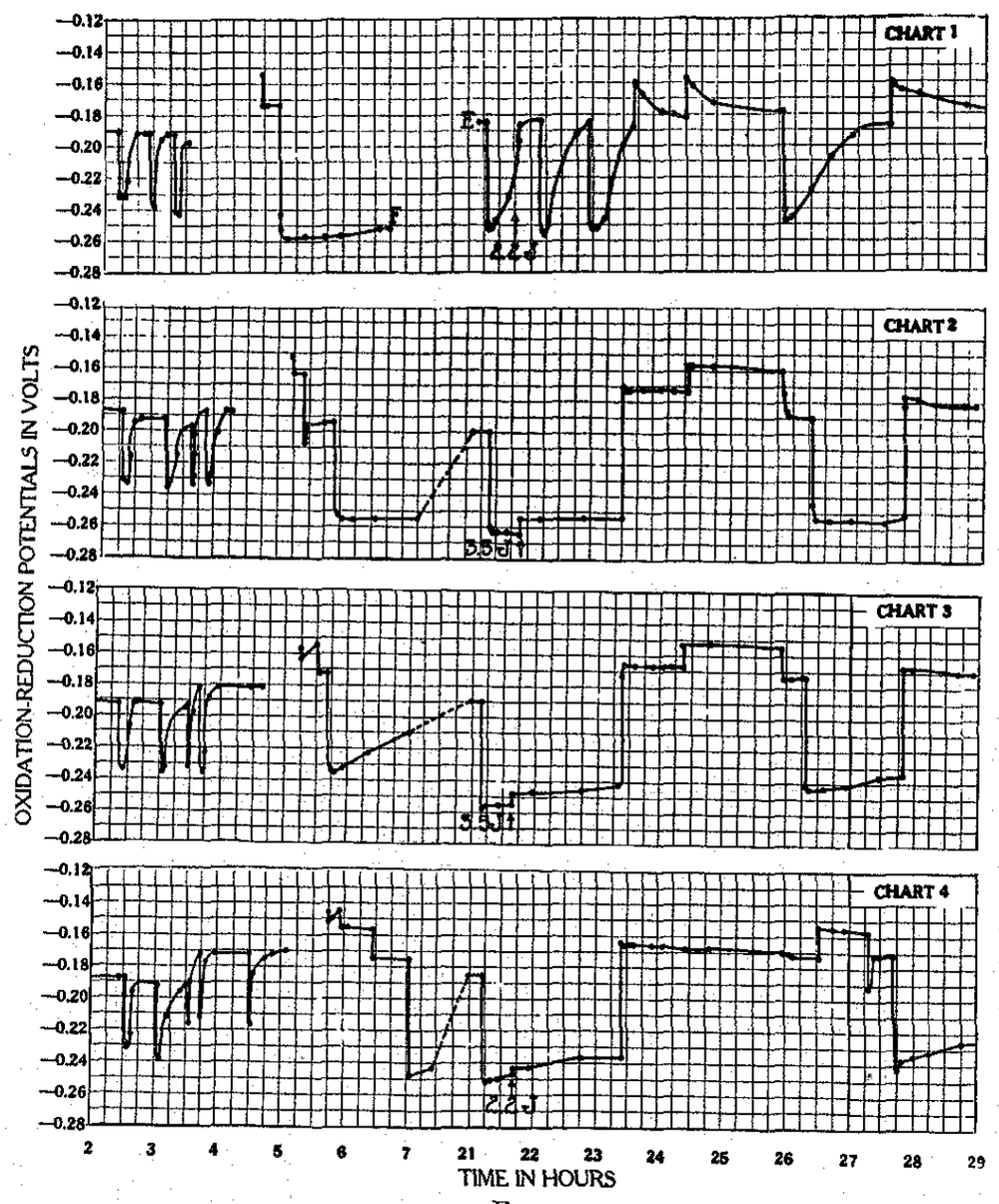


FIG. 1

After a few minutes the indigo carmine in each solution was reduced to a light yellow color. Nitrogen was again passed through the solutions about one hour after the peroxide had been added. The potential of all the solutions was then very near −0.19 volts. One cc. of 0.02 N reduced indigo was then added to each of the solutions; this produced the sharp increase in potential shown in the chart. After a few minutes the equilibrium point was reached and another cubic centimeter of reduced indigo was added.

The potential produced immediately after the addition was in the neighborhood of −0.24 volts. The solutions represented in Charts 1, 2, 3, 4, 5 and 6 were then boiled. The solutions represented in Charts 7 and 8 were not boiled. As soon as the solutions had again reached the temperature of the thermostat, 30°, reduced indigo was added. A slight oxidizing reaction was present in some of the solutions, requiring two and sometimes three additions of reduced indigo in order to produce a potential of −0.24. After a high

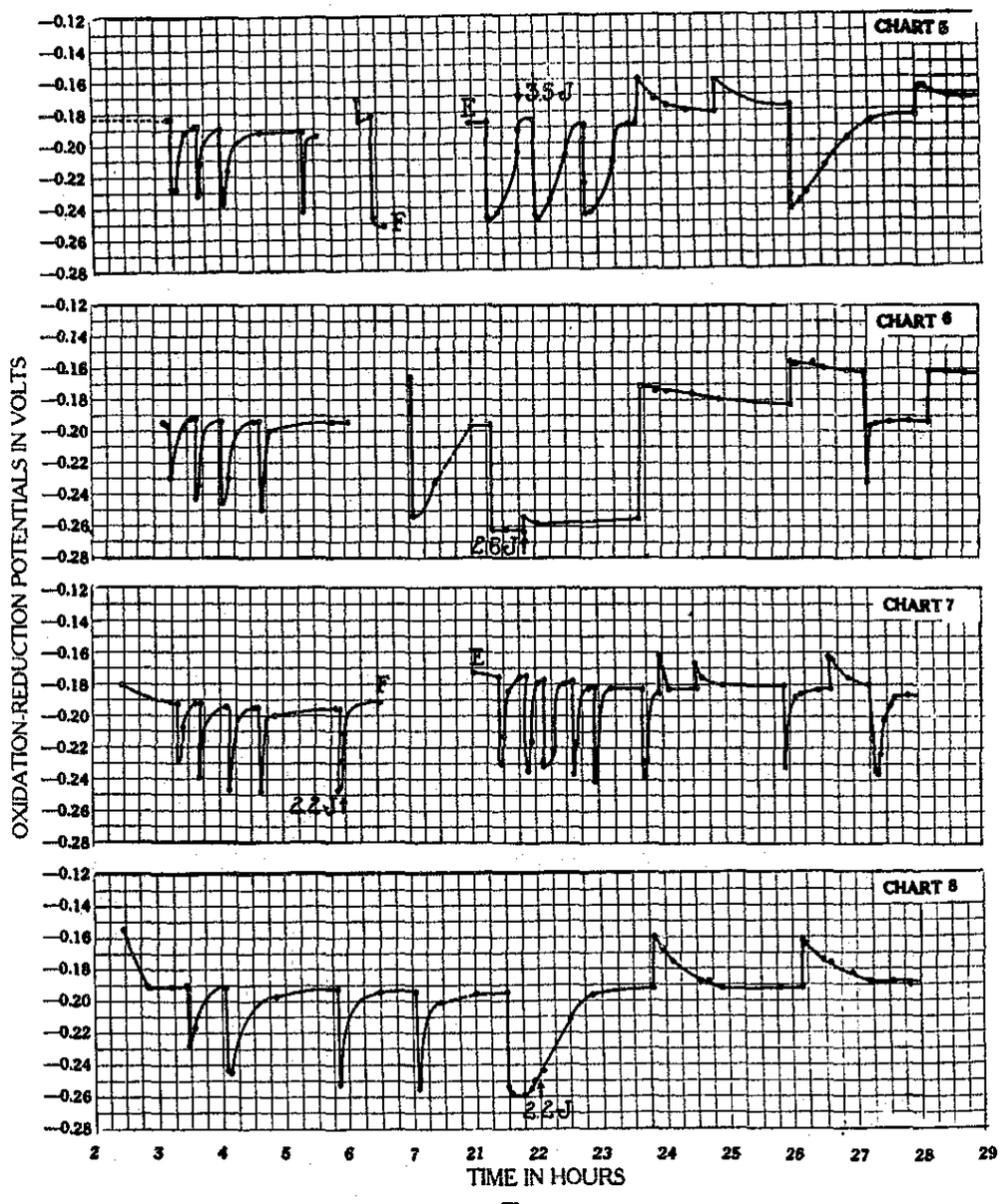


FIG. 2

potential, due to the reduced indigo, had been produced, no oxidation of reduced indigo occurred in those solutions which had been boiled and from which air was excluded. In Chart 1, 10 cc. of air was admitted to the electrode chamber after the potential of the solutions indicated that the reduced indigo had not been oxidized. The solution was then allowed to stand over night without nitrogen being passed through it. At the twenty-first hour the return to the equilibrium point showed that the reduced indigo had been oxidized,

and the addition of reduced indigo showed that the solution had marked oxidizing power. Also it was determined after the addition of indigo carmine that this solution would reduce indigo carmine. In the experiments depicted in Chart 2, all oxygen was excluded. After boiling, nitrogen was passed through the solution continually and the potential after the addition of reduced indigo showed that the solution had no oxidizing power. The added indigo carmine oxidized the reduced indigo and dropped the potential to approximately −0.15. The solution, however, was unable to reduce the indigo carmine. Subsequently by addition of 1 cc. of reduced indigo, the indigo carmine was reduced, and the addition of 1 cc. more raised the voltage to −0.25, but nothing was present in the solution which could oxidize the reduced indigo.

Charts 3 and 4 are similar to Chart 2. Chart 5 is a duplicate of Chart 1. Air was added after the boiling at six hours and forty minutes. The solution could both oxidize reduced indigo and reduce indigo carmine. Chart 6 is similar to Chart 2; all oxygen was excluded and oxygen-free nitrogen was passed through the electrode chamber continually after the solution had been boiled. Chart 7 shows the oxidizing and reducing power of a solution similar to the others except that it was not boiled and 10 cc. of air was admitted to the electrode chamber at the point indicated by six hours and thirty minutes on the chart.

Chart 8 is similar to Chart 7, except that no oxygen was admitted and the nitrogen passed through the solution continually for the entire thirty-one hours. Sulfuric acid, in the amount indicated, was added to neutralize the sodium hydroxide contained in the reduced indigo at the point indicated by "J". This produced a slight decrease in the reducing potential.

Influence of Hydrogen Ion Concentration

In order to prepare the oxygen addition-product in the solutions for Chart 9 to 16, 4 cc. 0.035 N indigo carmine and 1 cc. 0.1 N hydrogen peroxide were added to each. The solutions represented in Charts 9 and 10 were prepared by adding 176 mg. of reduced glutathione neutralized with sodium hydroxide to 100 cc. of a buffer at a pH of 6.4. The buffer contained 60 cc. of M/15 KH_2PO_4 and 40 cc. of M/15 Na_2HPO_4.

For Charts 11 and 12, 176 mg. of reduced glutathione was added to 100 cc. of phosphate buffer pH 5.9: 90 cc. of M/15 KH_2PO_4 and 10 cc. of M/15 Na_2HPO_4.

For Charts 15 and 16, 176 mg. of reduced glutathione was added to 100 cc. of buffer pH 3.8. This was prepared by adding 100 cc. of M/15 potassium acid phthlate to 5.3 cc. of 0.5 N hydrochloric acid.

Discussion of Details

The increases in potentials shown in the charts were produced by the addition of 1 cc. of 0.02 N reduced indigo, except where a number not followed by a letter above the curve indicates that a greater number of cubic centimeters was added. Indigo carmine was added in 1 cc. amounts, causing a decrease in potential.

The volume in cubic centimeters of 0.1 N sulfuric acid which was added is indicated by a number followed by the letter "J". The letters "E" and "F" in the charts designate the starting and stopping respectively of the flow of nitrogen through the electrode chambers. The times when reduced indigo and indigo carmine were added to the solution, which are not clearly indicated on the charts, are recorded in the following:

Chart 1: One cc. of reduced indigo was added at 2 hr. 12 min.; 2 hr. 42 min.; and 3 hr. 6 min. The solution was heated to boiling between 3 hr. 20 min. and 4 hr. 20 min. One cubic centimeter of reduced indigo was added at 4 hr. 20 min., and again at 4 hr. 42 min. The nitrogen was stopped and 10 cc. of air was added at 6 hr. 30 min. The nitrogen was started at 20 hr. 54 min. At 21 hr. 3 min. and at each of the points where subsequent sudden increases in the potential begin reduced indigo was added in 1 cc. portions. Indigo carmine was added to the solution at 23 hr. 24 min., at 24 hr. 16 min., and at 27 hr. 32 min.

Chart 2: The solution was heated to boiling at 4 hr. and was replaced in the thermostat and cooled at 4 hr. 58 min. One of cc. of reduced indigo was added at 4 hr. 58 min., at 5 hr. 10 min., and at 5 hr. 42 min. One cc. of reduced indigo was added at 25 hr. 50 min., but this was all oxidized by the indigo carmine which had not been reduced and a second cubic centimeter of reduced indigo was required at 26 hr. 15 min. in order to increase the potential to −0.25 volts. One cc. of indigo carmine was added at 27 hr. 44 min. and 1 cc. of reduced indigo at 28 hr. 52 min.

Chart 3: The solution was heated to 100° between 4 hr. 40 min. and 5 hr. 11 min. One cc. of reduced indigo was added at 5 hr. 15 min., at 5 hr. 31 min. and at 5 hr. 42 min. At 21 hr. 9 min. 1 cc. of reduced indigo was added. The decrease in potential at 24 hr. 18 min. was caused by 1 cc. of indigo carmine. One cc. of reduced indigo was added at 25 hr. 50 min. and at 26 hr. 15 min. The remaining additions of reduced indigo and indigo carmine are clearly indicated.

Chart 4: The solution was heated to 100° at 5 hr. 6 min. One cc. of reduced indigo was added at 5 hr. 45 min., at 5 hr. 55 min., at 6 hr. 24 min., and at 7 hr. 4 min. The increase in potential at 21 hr. 12 min. was produced by 1 cc. of reduced indigo. One cc. of indigo carmine was added at 26 hr. 31 min. One cc. of reduced indigo was added at 27 hr. 22 min. and at 27 hr. 42 min.

Chart 5: The solution represented in Chart 5 was boiled at 5 hr. 35 min. One cc. of reduced indigo was added to the solution after it was cooled at 6 hr. 12 min. and another cc. of reduced indigo was added at 6 hr. 24 min. Ten cc. of air was added and the solution was allowed to stand until the twenty-first hour. One cc. of indigo carmine was added at the twenty-eighth hour. The other additions of reduced indigo and indigo carmine in 1 cc. amounts are clearly indicated.

Chart 6: The solution represented in Chart 6 was boiled at 6 hr. 3 min. One cc. of reduced indigo was added at 7 hr. 3 min. after the solution had been brought to the temperature of the thermostat. One cc. of indigo carmine was

added at 23 hr. 38 min., at 26 hr. 2 min., and at 28 hr. 12 min. The increase in potential at 27 hr. 14 min. was produced by reduced indigo.

Chart 7: The solution represented in Chart 7 was not boiled. Ten cc. of air was admitted at 6 hr. 31 min. and the solution stood without nitrogen bubbling through it until the twenty-first hour. Each of the sudden changes from the equilibrium potential is produced by the addition of 0.02 N reduced indigo or 0.02 indigo carmine in 1 cc. portions.

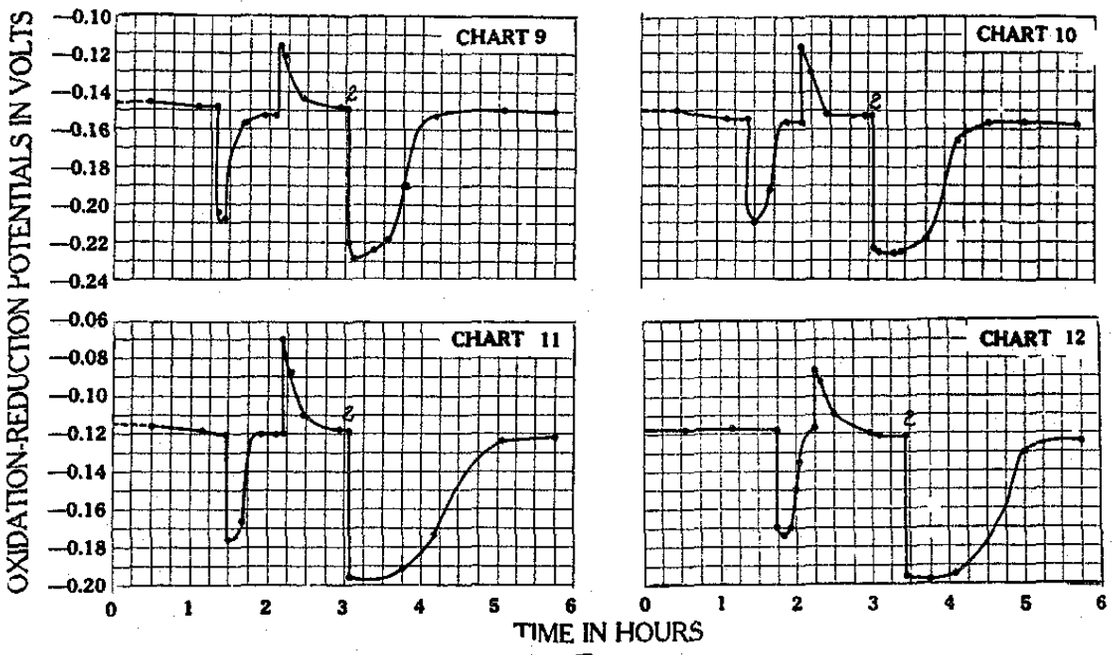


FIG. 3

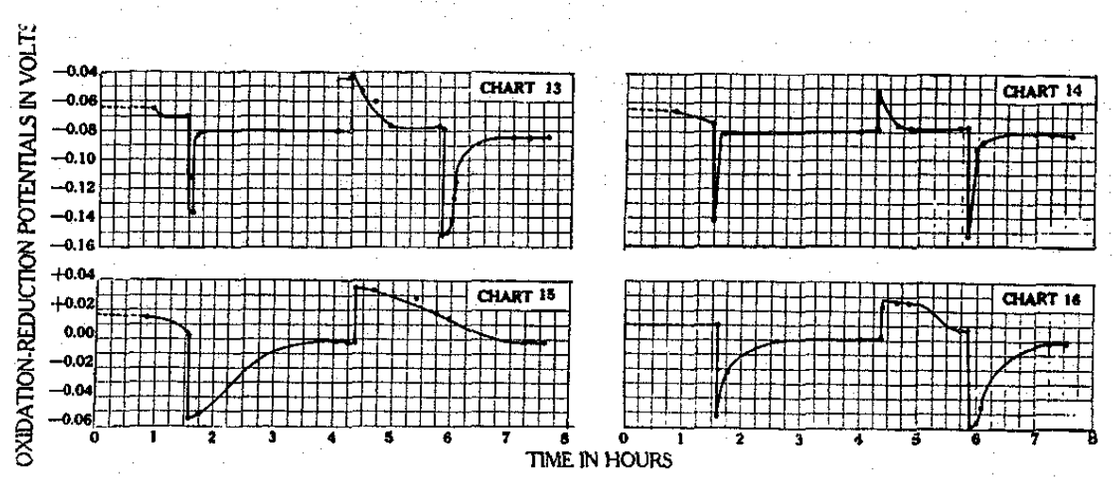


FIG. 4

Chart 8: The solution represented in Chart 8 was not boiled and nitrogen was passed through the electrode chamber without interruption. The reduced indigo and indigo carmine were always added in 1 cc. portions and the additions are clearly indicated on the chart. The solution was very sluggish in both oxidizing and reducing power after the twenty-first hour.

The addition of reduced indigo and indigo carmine to the solutions represented by Charts 9 to 16 is clearly indicated.

These results shown in Charts 9 to 16 are good evidence that the oxygen addition-product can be formed and will function at all hydrogen ion concentrations between a pH of 7.4 and 3.8. The velocity of reaction represented is, in distinction to the conceptions of Conant and Cutter[1], not an accurate criterion of the influence of hydrogen ion concentration alone, since the most important factor is the concentration of the oxygen addition-product, and by the method used there was no certainty that the same concentration of the essential transportation form was present in each of the solutions. Charts 13 and 14 show a more active oxidation of reduced indigo and reduction of indigo carmine than Charts 11 and 12, but the results are qualitative evidence that, as the concentration of hydrogen ion increased, the speed of oxidation of reduced indigo and the velocity of reduction of indigo carmine are decreased.

2.

In order to show the possible presence of a transportation system for oxygen in yeast and tissue suspensions the same apparatus was used for the measurements.

The tissues were prepared in the following manner. Liver and muscle of a rabbit bled and skinned under water in a large jar were removed and dropped separately into boiling water and boiled five minutes. The tissues being kept well submerged in water, they were then transferred to the large jar in which the pressing operations were carried out. The dimensions of the press were such that the pressed tissue and juice was delivered directly in the electrode chambers. A certain amount (8-9 g.) of the content of the press, measured by a corresponding number of turns (15), was pressed in the chambers while nitrogen was passed through the buffer solution which had previously been carefully deoxygenated.

The general manner of the execution of the experiments with yeast was identical with that described. Each of four electrode chambers were charged with 5 g. of yeast and boiled ten minutes. The highest oxidation-reduction potential of the suspension recorded after the addition of 4 cc. of 0.02 N indigo carmine was -0.1303 volt corresponding to a dark blue color which was unreduced after 21 hours.

A series of experiments were carried out with muscle and liver suspensions. As already indicated, no reduction of indigo carmine was observed since the average oxidation-reduction potential of the solutions was -0.1337 volt. In some cases reduced indigo was added to the solutions, in order to show its capacity to oxidize. After eight hours the solutions showed with liver an average oxidation-reduction potential of -0.2305 volt and with muscle pulp -0.2424 volt, indicating that no oxidation of the reduced indigo had taken place. These readings were also in good harmony with the fact that no indigo precipitate was observed.

Similar but less certain results were obtained when the solutions were tested for their capability to reduce methylene blue in the presence of glutathione. The solutions (controlled also in their behaviour toward a solution of

[1] J. B. Conant and H. B. Cutter: J. Phys. Chem., **28**, 1098 (1924).

indigo carmine) were prepared in a manner similar to that described, with the exception that the boiling was repeated. The solutions showed after six to seven hours an average oxidation-reduction potential of −0.0233 or −0.0432 volt and a slight but definite decolorization of 0.25 to 1.0 cc. of 0.01 M methylene blue solution.

These results might be regarded as an indication of the possible production of some −SH groups, by the thermostable system of Hopkins.

Summary

The essential oxygen addition-product which brings into equilibrium the reduced and oxidized form of sulfur compounds may be prepared at hydrogen ion concentrations between pH of 7.4 and 3.8, but the solutions are much less active at the lower pH values. The solutions can be reactivated, after destruction of the oxygen addition-product by heat, through the action of oxygen.

The experiments indicate that under the conditions obtaining, muscle, liver and yeast suspensions do not form reversible systems with oxidized glutathione after the suspensions have been heated to boiling. Whether a reversible system involving glutathione which is dependent on an oxygen transportation system exists in normal tissue has not been shown.

It is possible that the transportation system which was regarded as being responsible for oxidation-reduction processes in tissues or yeast may be different from the one in the experiments described in this paper.

The experimental part of this investigation was carried out with the assistance of Mr. D. F. Loewen, and was facilitated partially by grants of the International Education Board and the Physiological Institute, Tierärztliche Hochschule, Berlin.

THE EFFECT OF GELATIN UPON THE SIZE AND DISTRIBUTION OF MACROSCOPIC CRYSTALS GROWN FROM AQUEOUS SOLUTIONS

BY T. S. ECKERT AND W. G. FRANCE

In a previous article by one of us[1] it was shown that the presence of gelatin in the electrolyte used in the electrochemical precipitation of basic lead carbonate resulted in a marked decrease in the average size of the particles obtained and also produced a decided increase in the uniformity of these particles. Other work as yet unpublished has indicated that the average size and uniformity of particles produced by chemical precipitation is affected in a similar manner by the addition of colloidal substances and dyes. While as yet no complete explanation of the effect of gelatin on the size distribution of such particles has been made it is apparent from some work to be published later that the explanation is one of selective protective action.

The present investigation was undertaken in order to determine if any similarity of size distribution and uniformity of particles existed between electro-chemical and chemical precipitation on one hand and the growth of macroscopic crystals from aqueous solution on the other. Although the conditions may not be strictly comparable, it is evident that the forces affecting microscopic or macroscopic crystal growth ought to be the same and any factors that inhibit such growth ought to prevail whether or not growth takes place as the result of electro-chemical and chemical precipitation or as the result of growth from aqueous solution by evaporation.

In this work the effect of two grades of gelatin upon the size and the distribution of macroscopic crystals of copper sulfate and lead nitrate when grown from aqueous solutions is determined.

The procedure followed was analogous to that used by France and McBurney.[1] In brief it consisted in allowing a definite amount of the saturated salt solution to slowly evaporate at room conditions, the crystal nuclei that formed spontaneously being allowed to continue growth for a definite time interval. At the end of the growth period the dishes containing growing crystals were photographed and the negatives thus obtained were projected upon a calibrated screen from which the size and the distribution were determined.

Copper sulfate and lead nitrate were selected for study since both readily form large uniform crystals from aqueous solution. The material used was of the C. P. grade purified by recrystallization. Two grades of gelatin were used the one designated gelatin A containing 1.2% ash; and the other gelatin B containing 1.65% ash.

The solutions were prepared for crystallization by agitating a sufficient quantity of the finely divided salt with water, the temperature being kept

[1] France and McBurney: J. Am. Chem. Soc., 46, 540 (1924).

constant at 25°C. by means of a thermostat. In all cases agitation of the solution was continued until after prolonged stirring a quantity of excess salt remained undissolved. This insured a saturated solution. When gelatin was added to the solution, stirring was continued after the addition of the sol. The concentration of the gelatin was varied between 0 and 1%, the percentage basis being grams of gelatin for each 100 cc. of solution. Four 50 cc. portions of the filtered solution were placed in as many small, uniform, crystallizing dishes about 8 cm. in diameter. These had been previously placed in a constant temperature room which was kept at 27° C. ±.5°. Evaporation from the solutions produced crystal nuclei which were allowed to grow for a definite time interval which in all cases was twenty-four hours. Each gelatin concentration of a growth series had four duplicates and the growth in all dishes for all concentrations of gelatin in any one series began at the same time. Likewise the termination of the growth periods was simultaneous.

At the end of the growth period the dishes were covered with watch glasses and each in turn was photographed using a 4x5 plate camera equipped with a vertical rack and so adjusted that the crystal images on the plates had the same size as the original crystals. Care was taken to retain the original set up in order to obtain uniform magnification thruout.

The method of determining the size and distribution of the crystals was essentially that used by France and McBurney[1] and described by Green.[2] This consisted in projecting the negatives onto a calibrated screen such that a total magnification of 26 diameters was obtained. The size of the crystals so projected was measured directly on the screen by means of a calibrated scale. In the case of lead nitrate crystals, the average diameter was readily determined while with copper sulfate the longest dimension was used as an indication of relative size. The results for the growth in each dish were tabulated as shown in Table I and the number of crystals of each size were counted.

TABLE I

Record Sheet of Crystal Measurements
Copper Sulfate at 27°C. with .05% Gelatin B

1	2	3	4	5
m m.	F Frequency	F × m.m.	V	F × V²
1	0	0	0	0
2	5	10	3.4	57.8
3	6	18	2.4	34.6
4	7	28	1.4	13.7
5	10	50	.4	1.6
6	13	78	.6	4.7
7	11	77	1.6	28.2
8	3	24	2.6	20.2
9	3	27	3.6	38.9
Total	n = 58	312		199.7

[1] J. Am. Chem. Soc., **46**, 540 (1924).
[2] J. Franklin Inst., **192**, 637 (1921).

TABLE II

Summary of Crystal Size and Uniformity Coefficients

Crystals	% Gelatin	Average Size in m.m.	Uniformity Coefficient
Copper Sulfate	.0 Gelatin B	4.80	.29
" "	.05 " "	5.27	.32
" "	.1 " "	5.50	.29
" "	.2 " "	4.75	.24
" "	.3 " "	4.82	.32
" "	.5 " "	2.03	.93
Copper Sulfate	.0 Gelatin A	4.94	.21
" "	.05 " "	6.30	.25
" "	.1 " "	6.56	.24
" "	.3 " "	5.60	.33
" "	.5 " "	3.67	.85
Lead Nitrate	.0 Gelatin B	2.67	.26
" "	.1 " "	1.84	.49
" "	.3 " "	1.46	.53
" "	.5 " "	1.79	.56
Lead Nitrate	.0 Gelatin A	4.69	.21
" "	.05 " "	1.38	.61
" "	.1 " "	1.36	.65
" "	.3 " "	1.43	.76
" "	.5 " "	1.68	.48
" "	.7 " "	1.87	.53

In the record sheet indicated in Table I the column headed mm. represents the actual size of the crystals. Column 2 gives the number of particles of a given size while Column 3 is the product of mm. and frequency. Column 4 gives the variation in millimeters between the average size and the corresponding crystal size shown in Column 1. Column 5 is the product of Column 2, and the square of Column 4. Total values are indicated.

The average crystal diameter in any case is determined by dividing the sum of Column 3 by the total number of crystals which is the sum of Column 2. This may be represented by the expression $\frac{F \times mm.}{n}$ or from Table I $\frac{312}{58} = 5.38$ mm. The distribution of crystal size is given by the uniformity coefficient U which may be represented by the expression $U = \sqrt{\frac{N}{2FV^2}}$, where n is the total number of particles and FV^2 is the sum of Column 5. For the crystals indicated in Table I $U = \sqrt{\frac{58}{399.4}} = .38$

Table II includes a summary of the average values obtained for the growth of crystals of copper sulfate and lead nitrate. These results were obtained by averaging the data from the four dishes containing the same solution. The accompanying figures illustrate how gelatin affects the average size and the uniformity of the crystals so grown. Figures 1 and 2, with 3 and 4 show the results obtained for copper sulfate and lead nitrate when the respecitve series were grown at 27°C. These curves show that for each salt there is no decided difference in action for the two kinds of gelatin used.

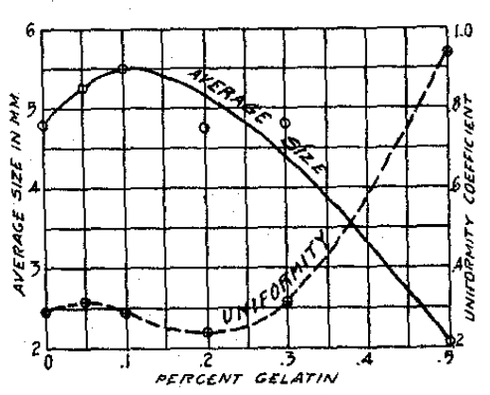


FIG. 1

Copper Sulfate—Gelatin B at 27°C. Curves for average size and uniformity.

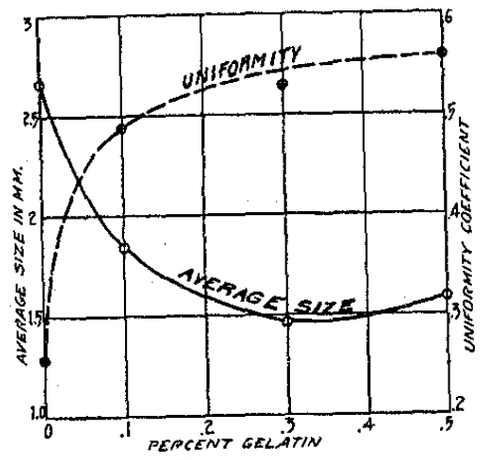


FIG. 3

Lead Nitrate—Gelatin B at 27°C. Curves for average size and uniformity.

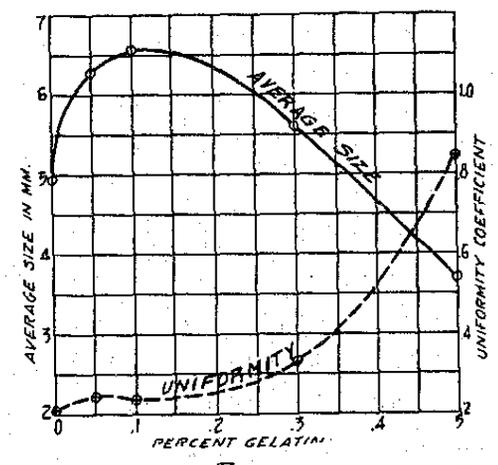


FIG. 2

Copper Sulfate—Gelatin A at 27°C. Curves for average size and uniformity.

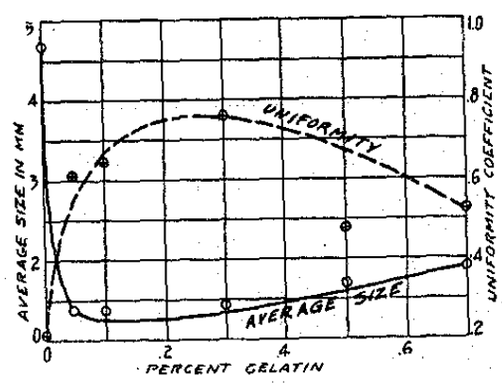


FIG. 4

Lead Nitrate—Gelatin A at 27°C. Curves for average size and uniformity.

The decided rise in the uniformity of the size of crystals obtained for lead nitrate as distinguished from copper sulfate may probably be due to the more uniform shape of these crystals since they crystallize in the regular system. That gelatin is more strongly adsorbed at some faces of copper sulfate than others has been indicated in some unpublished work and this may be a determining factor in the shape of the uniformity curves obtained.

From the curves included it is apparent that the average crystal size is reduced by the presence of small amounts of gelatin in the solution. At the same time a marked increase, in most cases, is noted in the uniformity of the

crystal size with increasing concentrations of gelatin. The irregularities in the curves may be due to the lack of exact control of all conditions affecting growth, such as humidity, the presence of dust particles, etc. In general, however, the experimental data leads to the conclusion that there is a decided similarity in the action of gelatin as affecting electro-precipitation and chemical precipitation on one hand and the spontaneous growth of macroscopic crystals from aqueous solution on the other.

The authors wish to thank Dr. P. W. Whiting of the Department of Biology at the University of Maine for the use of photographic equipment and Mr. L. D. Lebet who counted many of the projected plates.

Summary

1. The presence of gelatin in solutions of copper sulfate and lead nitrate has been shown to produce a marked decrease in the average size of the crystals obtained when growth is allowed to take place as the result of evaporation. At the same time increasing concentrations of gelatin increased the uniformity of the size of the crystals.

2. No decided differences were noted in the effect produced by the two grades of commercial gelatin used.

3. The results indicate a similarity in the action of gelatin as affecting microscopic crystals formed either by electro or chemical precipitation methods on one hand and macroscopic crystals grown from aqueous solution as the result of evaporation on the other.

The Chemical Laboratories of the University of Maine
and the Ohio State University.

MUTAROTATION. II

The relative velocities of mutarotation of α and β glucose: effect of acid and salt.

BY JOHN CLARK ANDREWS AND FREDERICK PALLISER WORLEY

The velocity of mutarotation of β glucose in water has been determined by Roux[1] and by Hudson and Dale[2], both of whom found that the velocity constant was approximately the same as that for the mutarotation of α glucose. We have unfortunately not had access to the original papers. On account of the large effect on the velocity produced by minute amounts of catalysts unavoidably present, there appeared to be a possibility of the agreement in the value of the two constants being accidental. A true comparison may, however, be made by comparing the velocities under similar conditions in the presence of a relatively large amount of catalyst sufficient to mask the effect of accidental impurities. We have consequently determined the velocities of mutarotation of both α and β glucose in aqueous solutions of hydrochloric acid of different strengths, under similar conditions. The concentration of acid varied from 0 to about 3 mols. of hydrogen chloride to 1000 mols of water.

The temperature of the determinations was 25°C.

The β glucose was prepared by a slight modification of Tanret's method.[3] A concentrated solution of α glucose was slowly evaporated to dryness during about seven hours at 112°C. The dried sugar was then dissolved in the smallest amount of hot water in a flask and the temperature raised to 112°. On the addition of a drop of cold absolute ethyl alcohol local crystallization commenced. The flask was then rapidly cooled under the tap and excess of cold absolute alcohol added with vigorous stirring. The β glucose immediately crystallized, was separated and dried as rapidly as possible, and stored in a waxed flask connected to a second flask containing phosphorus pentoxide. The product was nearly but not absolutely white. Its optical rotation found by extrapolation using the mercury green line was $[\alpha]^{25°C}_{5461} = 23.8°$. The values recorded by previous investigators are in terms of the D line of sodium. In terms of the mercury green line they are as follows: Tanret[4] 26.6, Simon[5] 26.0, Behrend[6] 24.4 and Hudson and Yanovsky[7] 22.4. The equilibrium rotation after mutarotation was 61.3 agreeing with the value 61.5 found on mutarotation of α glucose.

[1] Ann. Chim. Phys., (7) **30**, 422 (1903).
[2] J. Am. Chem. Soc., **39**, 320 (1917).
[3] Compt. rend., **120**, 1060 (1895).
[4] Compt. rend., **120**, 1060 (1895).
[5] Compt. rend., **132**, 487 (1901).
[6] Ann., **377**, 220 (1910).
[7] J. Am. Chem. Soc., **39**, 1013 (1917).

The velocity constants were calculated on a sixty second unit of time by the formula $k = \frac{1}{t_2 - t_1} \log_{10} \frac{a - x_1}{a - x_2}$ where "a−x" is the difference between the rotation at any time "t" and the final rotation at equilibrium. The results are given in Table I. in which the concentration of acid is expressed as the number of gram molecules of hydrogen chloride per 1000 gram molecules of water.

TABLE I

α glucose		β glucose	
Conc. of HCl.	$k \times 10^3$	Conc. of HCl.	$k \times 10^3$
0	9.6	0	9.7
0.64	16.0	0.54	14.8
0.65	17.4		
0.96	18.7	0.96	18.3
1.10	20.2	1.10	21.1
1.11	20.3		
1.78	25.5		
1.79	29.8	1.92	26.7
2.27	33.0		
2.28	30.9		
2.83	36.0		
2.91	36.9		

The results are shown graphically in Fig. 1 in which it is seen that the points for α glucose (o) and for β glucose (+) lie on the same curve, which is a straight line.

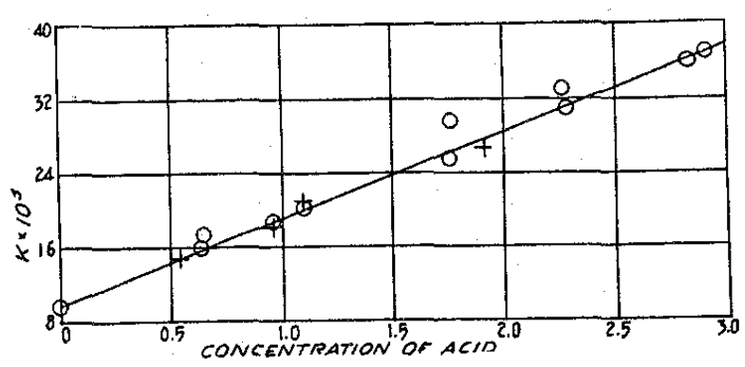


FIG. 1

The depression of the curve at very low concentrations of acid observed by Osaka[1], Hudson[2], Euler[3] and his co-workers and Kuhn and Jacob[4] was not observed. Further investigation on this point is desirable. The curve is in close agreement with the equation deduced by Hudson for the effect of acid

[1] Z. physik. Chem., **35**, 663 (1900).
[2] J. Am. Chem. Soc., **29**, 1571 (1907).
[3] Biochem. Z., **107**, 150 (1920); Arkiv Kem. Min. Geol., **8**, (No. 28), 1 (1923).
[4] Z. physik. Chem., **113**, 389 (1924).

and alkali on the velocity of mutarotation of α glucose. Kuhn and Jacob's equation does not fit the curve so closely. From the fact that the values of the constants for α and β glucose lie on the same curve it may be concluded that the velocity constants for the α and β forms of the sugar are identical under similar conditions, a conclusion of importance in considering the mechanism of the change.

Effect of Sodium Chloride on the Rate of Mutarotation

The influence of salts on the velocity of mutarotation has been studied by numerous investigators. In general an acceleration has been observed and has been attributed to the presence of acid or alkali. Conflicting results have been recorded in the case of neutral salts such as sodium chloride, some observers finding an increase in the velocity, others a decrease. It was desirable on theoretical grounds to ascertain the true effect of neutral salts and to this end the effect of specially purified sodium chloride on the velocity of mutarotation of α glucose in water has been examined.

Purification of Sodium Chloride

In order to avoid the presence of minute amounts of alkali frequently present in salt purified by the usual methods, the sodium chloride was purified by a method avoiding the application of heat. The purest sodium chloride obtainable by precipitation by hydrogen chloride was dissolved in the smallest amount of highly purified cold water and reprecipitated by the addition of purified ethyl alcohol. This process was repeated several times and the final product, after washing with absolute alcohol, was dried at 25°C.

The effect on the velocity of mutarotation of α glucose in water solution produced by this specially purified salt over a considerable range of concentration and also the effect produced by this salt after heating to 120°C are shown in Table II, in which the concentration of salt is expressed as mols. of sodium chloride to 1000 mols of water.

TABLE II

Conc. NaCl.	$k \times 10^3$	Conc. NaCl.	$k \times 10^3$
0.	9.6	1.89	9.71
0.84	9.78	3.09	9.71
1.79	9.80	3.64	9.99
1.83	9.66	4.88	10.20
1.87	10.30	8.63	9.67

It is seen that the neutral sodium chloride purified in the cold has no effect on the velocity of mutarotation. After heating to 120°, however, the salt has a distinct accelerating effect. The effect of salt after fusion was also observed and found to be very much greater. It must be concluded that the effect of sodium chloride observed by previous workers were due to the presence in the salt of either acid or alkali.

Summary

1. The velocity of mutarotation of α glucose and β glucose in aqueous solutions of hydrochloric acid has been determined over a considerable range of acid concentration. The velocity constants for both forms of the sugar lie on the same curve which is a straight line.

2. The effect on the velocity of mutarotation of α glucose in aqueous solution produced by specially purified sodium chloride over a considerable range of concentration has been examined. The salt was found to have no influence on the rate. The purified salt after heating to 120° had an accelerating effect.

We desire to express our indebtedness to the Royal Society for a grant to one of us (F. P. W.) towards the cost of polarimetric apparatus, and to the Duffus Lubecki Scholarship Fund for a Scholarship which enabled one of us (J. C. A.) to take part in the investigation.

Auckland University College,
University of New Zealand,
March 1, 1927.

AN IMPROVED HYDROGEN ELECTRODE VESSEL AND THE ELECTROMOTIVE FORCE OF THE MERCURY, MERCUROUS BROMIDE, BROMIDE ION ELECTRODE

BY ROSCOE H. GERKE AND JAMES R. GEDDES

Electromotive force measurements in dilute solutions require the highest refinement of technique. One of the principal difficulties is that the sensitivity of the galvanometer is reduced by the high electrical resistance of the galvanic cell, which is in the same circuit. This difficulty has been surmounted by Linhart.[1] His measurements are undoubtedly the best in the field of extremely dilute solutions. His cell, although admirably adapted to his research, is unsuitable with respect to two features in the present investigation.

It has been observed[2] that a suspension of calomel and mercury in dilute potassium chloride solution soon reacts alkaline to phenolphthalein. The mercury was assumed to have been oxidized by dissolved air. This reaction would cause alkalinity and also a decrease in the chloride ion concentration. This decrease in chloride ion concentration would affect the potential of the calomel electrode especially in dilute solution. In order to prevent atmospheric oxidation of the mercury and also to prevent mercurous ions from diffusing to and poisoning the hydrogen electrode the following cell was constructed.

Description of Hydrogen Electrode Vessel.

The general features of the Pyrex electrode vessel are shown in Fig. 1. Electrolytic hydrogen is saturated with water vapor in the bulbs, A; introduced into the cell thru the perforated nozzle, B. It then passes thru the solution and past the platinized platinum electrodes, C, and out of the cell through the trap, D. The calomel electrode, E, is filled thru the side tuber, F. The important feature of the cell is the platinum gauze, G, which supports very carefully cleansed Standard Ottawa Sand, H. The purpose of the sand is to prevent diffusion or convection of mercurous ions from the calomel electrode. In filling the cell electrolyte is poured in to the level, I. When the solution has become saturated with hydrogen, it is withdrawn from the cell thru F to the level, J. This operation replaces the original electrolyte in the calomel electrode with air free electrolyte. In this manner the high conductivity of the cell was maintained, the oxygen was removed from the calomel electrode and the diffusion of the mercurous ions to the hydrogen electrodes was prevented.

Filling the Electrode Vessel.

The technique of filling the electrode vessel consisted in first introducing the mercury thru the side arm, F. Then the electrolyte is introduced thru

[1] Linhart: J. Am. Chem. Soc., **41**, 1175 (1919).
[2] Gerke: J. Am. Chem. Soc., **44**, 1684 (1922).

the top opening of the cell. A large bubble of air can be removed from the lower side of the platinum gauze by sucking sharply on a pipette which rests on the upper surface of the gauze. Sand is poured on the gauze from the top filling the cell to the nozzle, B. The mercury, mercurous bromide suspension is introduced with a pipette through the side tube, F. After the upper

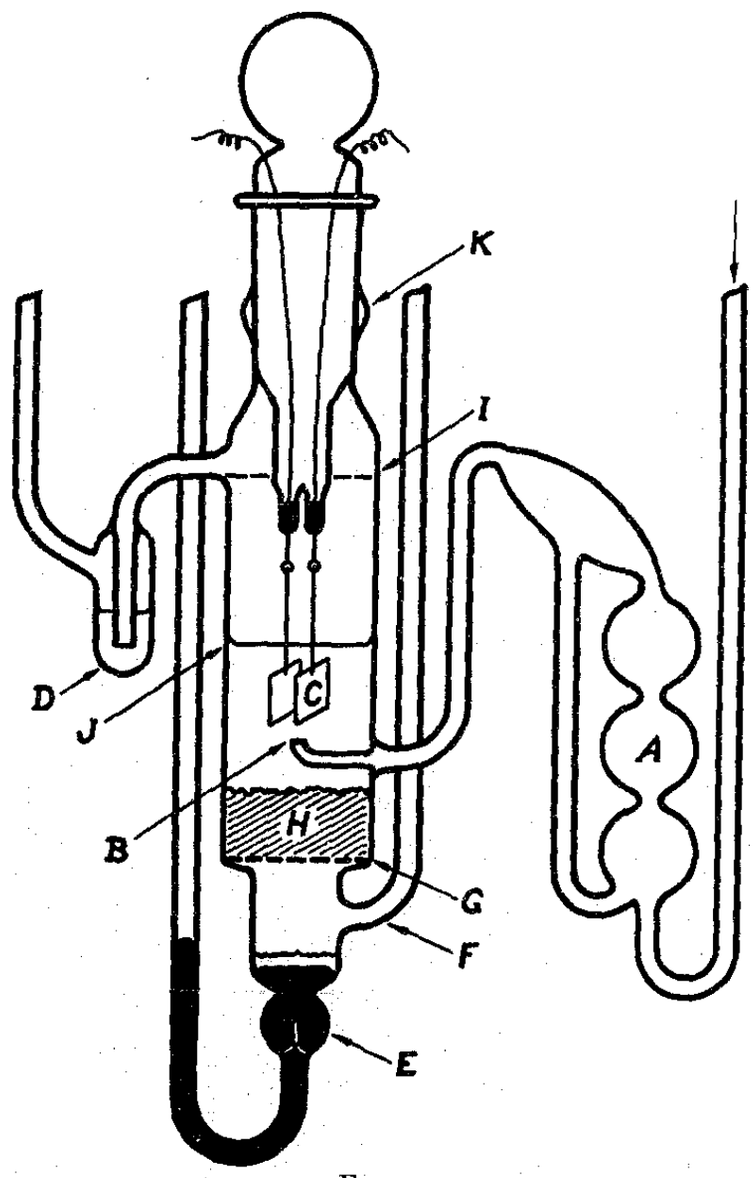


FIG. 1

electrolyte is saturated with hydrogen, electrolyte is slowly removed through the side tube, F, in order to replace the electrolyte in the calomel electrode with air-free electrolyte. The side tube, F, is closed by heating with the flame of a hand torch.

Experimental Results.

The cell, $H_2|HBr\ 0.10015F, Hg_2Br_2(S)|Hg$ was made and placed in an oil thermostat at 25.0°C. The electromotive force was measured with a Leeds Northrup Type K Potentiometer. The standard cells were purchased from Eppley. Edison storage cells were used for a working battery.

Five cells were constructed before reproducible and constant results were obtained. It was observed that three precautions had to be observed. (1) Daylight blackened the mercurous bromide suspension, which made it necessary to cover the thermostat with black cloth. (2) The electromotive force of the cells permanently diminished after cell electrolyte was removed through the side tube, F. This diminution of electromotive force was greater for older preparations of the mercury, mercurous bromide suspensions. This was attributed to oxidation of the mercury and consequent decrease in bromide ion concentration. This effect was greatly diminished by using freshly prepared and freshly washed mercury, mercurous bromide suspensions. (3) The electromotive force of the cells remained constant for about two days and then slowly decreased till it was evident that the hydrogen electrodes were badly poisoned. This difficulty was remedied by keeping the side tube,

TABLE I

Electromotive Force of the Cell, $H_2(g)|HBr\ 0.10015, Hg_2Br_2(s)|Hg(l)$-at 25.0°C.

Time in hours		Barometric Pressure m.m.	Electromotive Force, Volts. Number 1 observed	Number 1 760 mm, H_2	Number 2 Observed	Number 2 760 mm, H_2
0	(3)					
10			0.2720		0.2720	
20.5			0.2722		0.2722	
21	(4)					
25.5		766.3	0.26864	0.26894	0.26863	0.26893
34		768.7	0.26871	0.26897	0.26872	0.26898
48		771.2	0.26870	0.26892	0.26870	0.26892
52		768.3	0.26863	0.26890	0.26862	0.26889
55.2		767.5	0.26856	0.26884	0.26856	0.26884
117.5		760.3	0.26803	0.26844	0.26802	0.26843
0	(5)					
11			0.2695			
17.5			0.2693			
18.0	(4)					
18.5		749.3	0.26798	0.26857	0.26800	0.26859
26.5		750.1	0.26762	0.26820	0.26760	0.26818
37.5		751.7	0.26797	0.26852	0.26796	0.26851
40.5		752.0	0.26787	0.26841	0.26785	0.26840
49.5	(6)	753.4	0.26797	0.26860	0.26797	0.26860
60.25		754.3	0.26798	0.26849	0.26799	0.26850
63.75		754.4	0.26800	0.26851	0.26800	0.26851

(3) Hydrogen started. Fresh Hg_2Br_2 prepared in dark. Fresh H_2 electrodes. Thermostat in light.
(4) Electrolyte removed thru tube, F.
(5) Hydrogen started. Fresh Hg_2Br_2 prepared in dark. Thermostat covered with black cloth. Fresh H_2 electrodes.
(6) Hydrogen electrode 1 replaced.

F, completely filled with electrolyte so that the bubbling of the hydrogen would not cause the electrolyte to move slightly back and forth thru the sand.

Cells 6 and 7 were constructed with due respect to the precautions listed above. The results are shown in Table I.

Discussion

The first cell in Table I gives an electromotive force about 0.4 millivolt higher than the second cell. This difference is probably due to a greater degree of oxidation of the mercury in the mercury, mercurous bromide suspension before filling the cell. The first cell also shows a slow trend in the value of the electromotive force, which may be due to either the effect of light or a very slight poisoning of the hydrogen electrode. The second cell which was more carefully assembled and kept in the dark does not exhibit any trend in two and one-half days.

The best value of electromotive force[1] for the cell, H_2(1 atm)|HBr 0.10015 F, Hg_2Br_2(s)|Hg(l) is 0.268_5 volts from these measurements.

The electromotive force for the cell, H_2(1 atm)|HBr ($a_2 = 1$), Hg_2Br_2(s)|Hg(l), computed from the value 0.2685 volts and the activity coefficient 0.814[1] for tenth formal hydrobromic acid, is 0.139_6 volts, and the potential of the electrode Hg(l), Hg_2Br_2(s), Br^- is -0.139_6 volts.

Summary

(1) An improved hydrogen electrode vessel has been described.

(2) The potential of the electrode Hg(l)|Hg_2|Br_2(s)|Br^- has been found to be -0.139_6 volts.

Forest Hills, Long Island, N. Y.
Gloucester, Mass.

[1] The same conventions as to sign of electromotive force are used as those employed by Lewis and Randall in "Chemical Thermodynamics and the Free Energy of Chemical Substances" (1922).

SOME VAPOUR PRESSURES AND ACTIVITIES OF AQUEOUS SOLUTIONS OF SODIUM SILICATES

BY A. N. C. BENNETT

R. W. Harman[1] has given a brief summary of the work which has been done on aqueous solutions of sodium silicates in the first paper of a series.

The object of this work was to determine the dew-point lowerings of various aqueous solutions of sodium silicates and of sodium hydroxide, by a method devised by A. C. Cummings[2], and improved by McBain and Salmon[3]. From these measurements some corresponding vapour pressures of the solutions, and activity coefficients of the solutes have been obtained.

Apparatus

The apparatus used was similar in many respects to that used by McBain with the addition of a stirrer driven electromagnetically to stir the liquid and air space inside the vessel.

The dimensions of the silver tube were 12 cms. long and 3 cms. in diameter. The lower end which was sealed was as thin as possible and highly burnished. The glass vessel was shaped at the mouth to take a rubber stopper and to withstand a vacuum. To keep the apparatus at constant temperature a glass faced thermostat was employed. By means of an electric thermoregulator with a Gouy adjustment[4] and a good stirrer the temperature of the thermostat was maintained, so that no change was observed on a Beckmann thermometer. The temperature of the silver tube was recorded by a Beckmann thermometer inserted in it and was controlled by circulating water through the tube from an auxiliary thermostat the temperature of which could be slowly changed.

Experimental Procedure

The glass vessel was cleaned between each experiment with caustic soda and chromic acid, and was finally washed with distilled water. Before an experiment the silver tube was polished and part of the tube rendered passive to dew formation by dipping the tube filled with hot water into boiling pure distilled water. After this treatment no dew was deposited on the surface which had been immersed and consequently the appearance of a well-defined line across the silver tube was the first indication of dew. Closer and more consistent readings were obtained in this manner, for a comparatively large quantity of moisture must be deposited before dew can be seen.

50 cc. of solution, the dew-point of which was to be measured, were poured into the glass vessel and the silver tube, filled with water at 80°C,

[1] J. Phys. Chem., **29**, 1155 (1925).
[2] J. Chem. Soc., **95**, 1772 (1909).
[3] Proc. Roy. Soc., **97A**, 44 (1920).
[4] J. Am. Chem. Soc., **42**, 60 (1920).

inserted into the top of the glass vessel. The apparatus was then evacuated to about 3 cms. pressure, measured by a manometer connected between the pump and apparatus. With the Beckmann thermometer inserted in the silver tube, the whole apparatus was immersed in the glass faced thermostat which was kept at 61.5°C. Water at 65°C was then circulated through the silver tube from the auxiliary thermostat, and the solution left to attain the temperature of the thermostat for one hour.

Dew-point readings were then obtained by alternately slowly lowering and raising the temperature of the silver tube until dew appeared and disappeared.

The temperatures of appearance and disappearance of dew should theoretically be the same, but owing to the difficulty of detecting the first and last traces of dew, and because of hysteresis effects (i.e. lag of temperature between the outside and inside of the silver tube, and delay of water vapour reaching equilibrium with the solution), this is not found practically. The mean of about eight up and down readings was therefore taken as the dew point of the solution.

To test the method and apparatus, H_2SO_4 solutions were examined at 25°C. The results obtained compared closely with the extrapolated results of J. N. Brönsted[1].

The sodium silicate solutions used were commercial ones. Some pure sodium metasilicate was prepared by the method of Vesterberg[2]. Solutions of this salt however gave practically identical results with commercial solutions to which the requisite amount of NaOH had been added. The commercial solutions contained sodium silicates of varying ratio Na_2O to SiO_2, with impurities of iron, aluminium, and traces of calcium, magnesium, and potassium[3].

The readings first obtained were inconsistent and possible causes of trouble such as the surface of the silver tube, the action of the silicate on the glass, heat radiation from the thermostat heater, and pressure of the air in the apparatus were investigated. In the latter case the best readings were obtained, when the partial pressure of the air was equal to or less than the pressure of the water vapour. At atmospheric pressure at 60°C there was too great a difference between the up and down readings. It was thought however that the chief trouble was a lag in the formation of dew. This might have been caused by:

(a) Formation of a skin on the surface of the solution.

(b) Layers of solution at different concentrations due to the viscous nature of the solution.

(c) The dew which is evaporated from the silver surface being deposited on the walls of the glass vessel instead of on the surface of the solution.

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[1] Z. physik. Chem., **68**, 693 (1910).
[2] Eighth Int. Congress Appl. Chem., **2**, 235 (1912).
[3] Harman: J. Phys. Chem., **29**, 1155 (1925).

To eliminate these possible irregularities some form of agitation was necessary. Shaking the apparatus was tried and found to affect the results. It was finally decided to stir the solution and vapour space. Since the apparatus was evacuated, a form of electromagnetic stirring was employed.

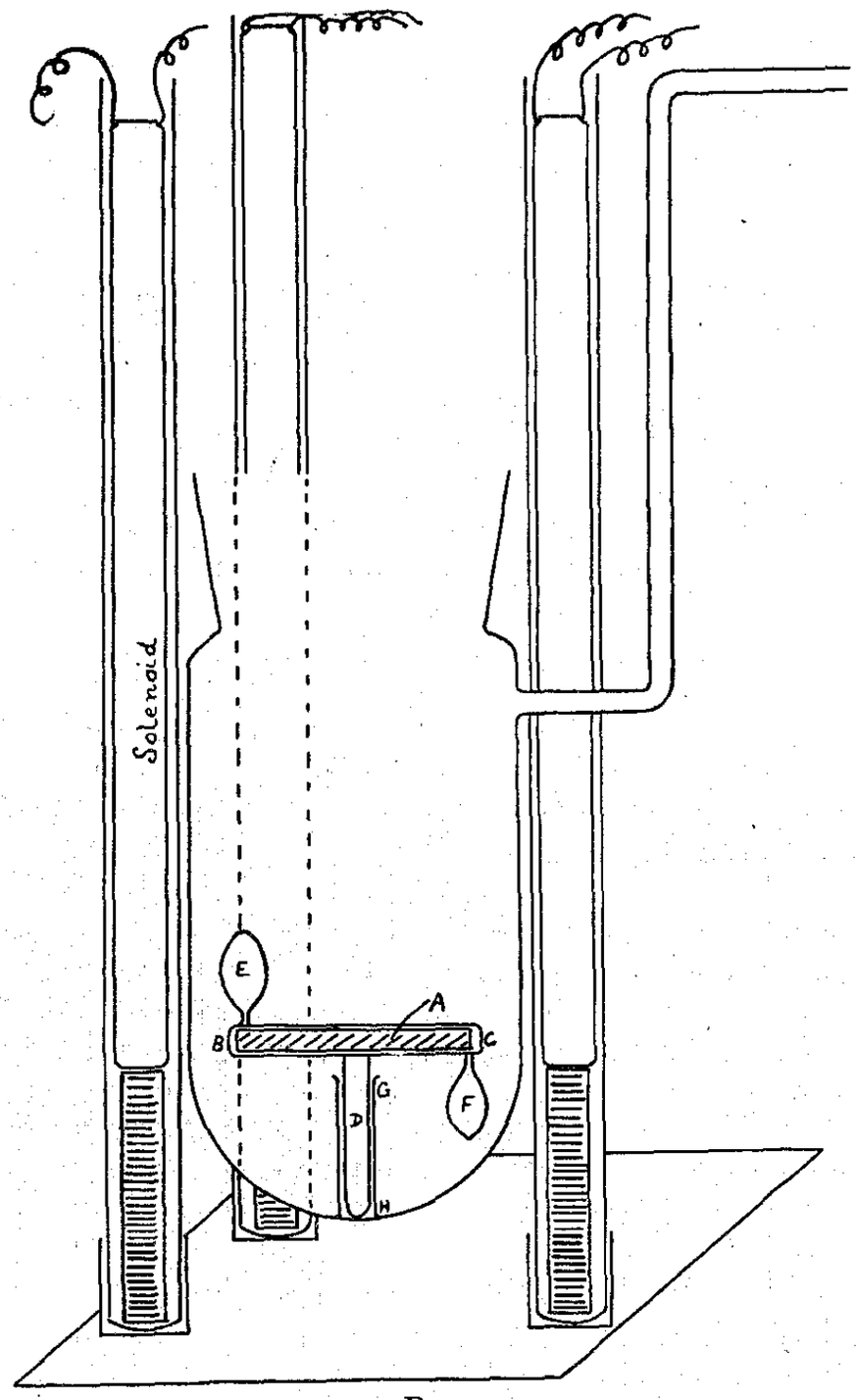


FIG. 1

The Electromagnetic Stirrer

Fig. 1 shows the type of stirrer used. A is a steel cylindrical core about 3 cms. long and 0.3 cms. in diameter sealed inside a piece of glass tubing. BCD is a glass rod sealed on to the middle of BC. E and F are glass vanes

sealed one on each end of BC in opposite vertical directions. D serves as a spindle about which E and F revolve. GH is a short glass tube fused into the bottom of the glass vessel, and is fixed in a vertical position, thus affording a bearing in which D can revolve freely.

The stirrer enclosed inside the glass apparatus was made to revolve in a horizontal plane by the production of a rotating magnetic field in the same plane. The rotating magnetic field was produced by alternating magnetic forces produced in three vertical electromagnets placed outside the glass apparatus (as shown) with the lower extremities in the same plane as the steel rod in the stirrer and equilaterally spaced.

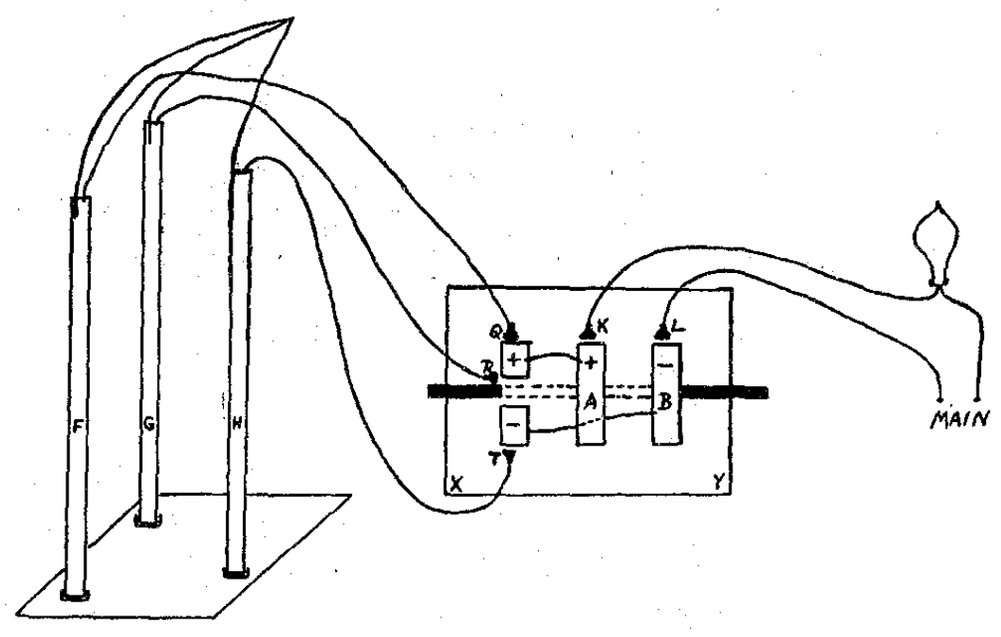


FIG. 2

Fig. 2 shows the design of the apparatus used to produce the alternating magnetism. XY represents a revolving split ring commutator. It has two brass half rings mounted on a cylindrical block of ebonite in such a way that there is a gap between their ends on either side of the cylinder. These two half rings are connected to two whole brass rings mounted on the same cylinder of ebonite. The cylinder is mounted on an axle about which it rotates. Two brushes K and L make contact with the rings A and B respectively, and by means of these brushes and rings, the two half rings are connected through a resistance to the positive and negative terminals of the main circuit. Three brushes Q, R, T, are fixed at equidistant points on the cylinder, and make and break contact with the half rings. The brushes are connected to the corresponding wires of the three solenoids, F, G, and H, the other three corresponding wires of the solenoids being connected together.

The solenoids consisted of soft iron cylindrical cores 1 cm. in diameter and 9 ins. long, and were wound with insulated copper wire. They were protected from the water in the thermostat by being supported in glass tubes sealed at one end.

When the apparatus is started, let us assume that the two brushes Q and R are touching the positively charged half ring, and the other T is in contact with the negatively charged half ring. In this way the two solenoids F and G are similarly magnetised, the other H is magnetised in the reverse way. Thus in the horizontal plane of the stirrer there are two N poles and one S pole and the stirrer sets with one end pointing towards H. As the commutator revolves the brush R will break contact with the half ring, and the solenoid G will be demagnetised. The stirrer then moves through an angle of 30° and sets parallel to the line joining FH. When the brush R makes contact with the half ring, there is one N pole (solenoid F) and two S poles, and the stirrer moves through another angle of 30° and points towards F. In this way the stirrer rotates at half the speed of the commutator which is driven by a motor of adjustable speed.

The introduction of the electromagnetic stirrer made a considerable difference in the results. A comparison of the dew-point readings for the same solution obtained with and without the stirrer are shown below. The readings given are those obtained on the arbitrary scale of a Beckmann thermometer.

Readings taken without using stirrer		Readings taken using stirrer	
Temperature Lowered	Temperature Raised	Temperature Lowered	Temperature Raised
1.23		1.43	
	1.34		1.50
1.25		1.47	
	1.34		1.15
1.25		1.49	
	1.40		1.53
1.33		1.49	
	1.35		1.52

Sets of dew point readings were taken for different sodium silicate solutions, and for caustic soda. For each ratio of Na_2O to SiO_2 five or six solutions of different concentrations were prepared. Two or three sets of readings for each solution were taken, and the mean of the results so obtained was taken as the true dew point lowering for the solution.

In Table I the results are shown with the concentration expressed in molality (i.e. gram mols of Na_2O per 1,000 grms. of water) and the dew point lowerings given in degrees Centigrade. The concentration is given in the first vertical column under M, and the dew-point lowerings are given for the various ratios of Na_2O to SiO_2, where 1 : 0 represents caustic soda.

TABLE I

M	1:0	1:0.5	1:0.87	1:1	1:1.4	1:2	1:3.2	1:3.95
1.5	2.40°	1.74°	——	1.35°	1.06°	0.75°	0.48°	0.41°
1.0	1.51°	1.19°	0.88°	0.92°	0.74°	0.56°	0.35°	0.29°
0.5	0.75°	0.60°	0.46°	0.46°	0.37°	0.30°	0.19°	0.15°
0.3	0.45°	0.37°	0.28°	0.27°	0.22°	0.19°	0.12°	0.10°
0.2	0.29°	0.25°	0.19°	0.18°	0.14°	0.13°	0.08°	0.07°

Activity Coefficients of Caustic Soda and Sodium Silicate Solutions

From the dew-point lowerings obtained, the activity coefficients of the caustic soda and sodium silicate have been determined by the method used by Lewis and Randall, and applied by them to solutions of sulphuric acid[1]. The equation obtained by them is:

$$\int d\left(\log \alpha_2\right) = -\int \frac{N_1}{N_2} d\left(\log \frac{p_1}{p_0}\right)$$

N_1/N_2 was plotted against p_1/p_0. The antilogarithm of the area under the curve between two values of N_2, one of which was arbitrarily fixed, gave a value proportional to α_2. It was assumed that the number of ions produced in solution was four[2]. Hence the fourth root of the above antilogarithm was calculated and this divided by the molality gave a value $K\gamma$ proportional to the activity coefficient γ. Values of $K\gamma$ were similarly obtained for several concentrations with the same arbitrarily fixed value of N_2.

From vapour pressure measurements it is inaccurate to determine K from $K\gamma$ by extrapolation to infinite dilution. In this work K was obtained by comparing values of $K\gamma$ obtained with the values of γ given by Harned[3] for caustic soda, and Harman[4] for sodium silicates. The concentration chosen for calculating K was in every case 0.5 molal. The curves, Fig. 3, obtained for γ against concentration are shown with those obtained by Harned and by Harman. For the more dilute and more concentrated solutions of NaOH the values obtained do not agree. There is an approximate agreement over a small concentration range for sodium silicates, but Harman has no figures to compare with the results obtained for the more concentrated solutions.

Discussion of the Method

As regards the improvement shown by the introduction of the stirrer in the dew-point apparatus, it is interesting to note that the analogous result was obtained by Jablczynski and Kon[5] in working on the elevation of boiling point method. They obtained their best results when their stirrer was making 2,000 revolutions per minute. They also state that a change in surface tension did not affect the results whereas it has a marked effect in the ordinary Beckmann determinations.

In the present work the supercooling effect has been lessened. The difference between the up and down readings was usually 0.02–0.03°C., whereas typical results given by McBain and Salmon for soaps show a difference of 0.06–0.07°C. The skin effect which was noticed in the earlier work was not observed in the later experiments in which the electromagnetic stirrer was

[1] Lewis and Randall: "Thermodynamics", 268, 331 (1923).
[2] Harman: J. Phys. Chem., **31**, 363 (1927).
[3] J. Am. Chem. Soc., **47**, 676 (1925).
[4] J. Phys. Chem., **31**, 365 (1925).
[5] J. Chem. Soc., **123**, 2953 (1923).

used. The speed of the stirrer was about 50 revolutions per minute, since splashing was feared from too vigorous stirring. It is possible however, that faster stirring would have produced better results, if the splashing could have been avoided.

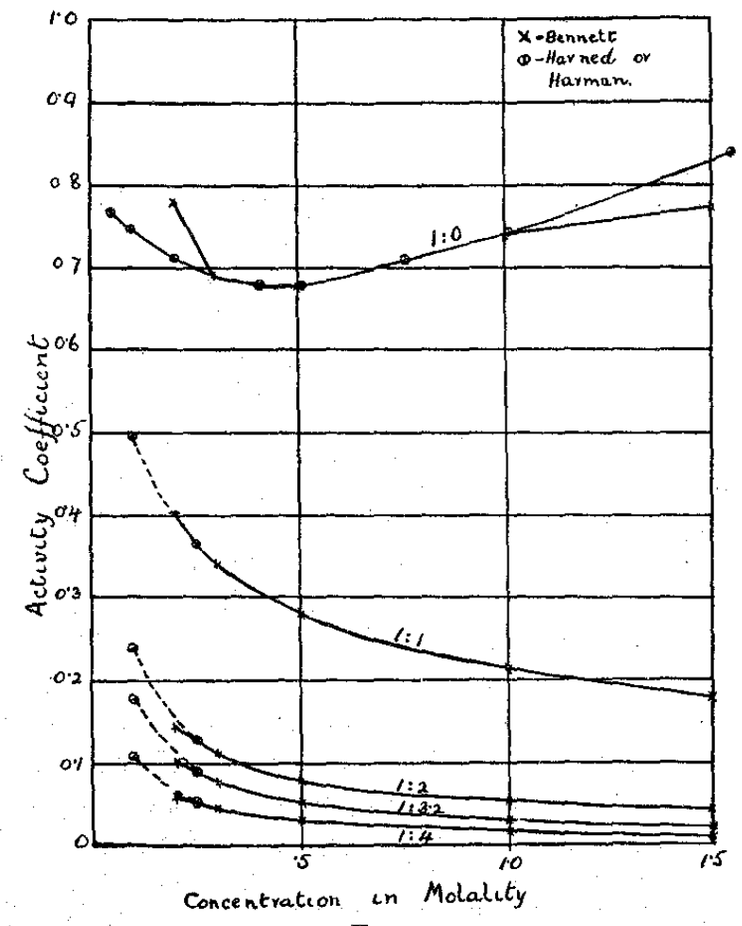


FIG. 3
Activity Coefficients against Concentration.

Summary

1. The dew-point lowerings of aqueous solutions of sodium silicates, and sodium hydroxide have been measured for solutions varying in molar ratio of Na_2O to SiO_2 from 1:0 to 1:3.95.

2. From these values activity coefficients of the solutes have been calculated, and have been compared with the values obtained by Harned for sodium hydroxide, and Harman for sodium silicates.

3. An electromagnetic stirrer has been devised for stirring the solution in a partial vacuum and by its introduction more reliable and concordant results were obtained.

The author wishes to express his thanks to Prof. F. G. Donnan, at whose suggestion the research was started, for his kind assistance and advice, and to Messrs. Brunner Mond for supplying the various solutions of sodium silicate.

The Sir William Ramsay Inorganic and Physical Chemistry Laboratories,
University College,
London.
February 1, 1927.

THE THICKNESS OF ADSORBED VAPOR FILMS*

BY J. C. W. FRAZER, W. A. PATRICK AND H. E. SMITH

The following experiments are an account of a series of investigations which were carried out with a view of ascertaining the thickness of the adsorbed films on *plane* surfaces. At the present time the phenomena of adsorption are theoretically classified by means of three distinct and unrelated generalizations. The unimolecular layer theory of Langmuir, the multi-molecular layer theory of Eucken-Polyani, and the capillary theory of Zsigmondy. The phenomena are so vague and uncertain that we find all three theories enjoying considerable vogue, each claiming to be applicable to certain experimental conditions. The uncertainty and modesty of the various proponents of the above theories is largely due to the difficulty of interpreting the various experimental results on the basis of any one theory. For example we find that Langmuir[1], and Carver[2] experimentally prove that the adsorbed layer is unimolecular in thickness. On the other hand Warburg and Ihmori[3], Pettijohn[4], Briggs[5], D'Huart and Hackspill[6], and McHaffie and Lenher[7] submit equally conclusive experimental evidence that shows that the adsorbed film is multimolecular in thickness on plane surfaces. This disagreement is not however considered serious by reason of the fact that the experimental conditions were not the same in the above experiments. It is generally believed that the unimolecular adsorbed film is to be found under low equilibrium pressures or at temperatures high above the critical temperature. On the other hand it is thought that the multimolecular layer is formed at pressures close to the saturation pressure. However the two phenomena are by no means clearly defined and there remains a chaotic condition as far as the quantitative aspect of the question is concerned.

One of the authors of this paper has for years held the opinion that the capillary theory is the most promising for explaining the phenomena of adsorption of vapors by porous bodies. It was also clearly recognized that the classical theory of capillarity was inadequate to account for the experimental adsorption results. Experiments were accordingly inaugurated in this laboratory to test the validity of the Lord Kelvin relation that governs the relation between the vapor pressure of a liquid and its radius of curvature. The results of these experiments (unpublished) were so encouraging that our belief in a modified capillary theory of adsorption was greatly strengthened.

* Contribution from the Chemistry Laboratory of Johns Hopkins University.

[1] Langmuir: J. Am. Chem. Soc., **38**, 2221 (1916); **40**, 1361 (1918).

[2] Carver: J. Am. Chem. Soc., **45**, 63 (1923).

[3] Warburg and Ihmori: Wied. Ann., **31**, 1006 (1887).

[4] Pettijohn: J. Am. Chem. Soc., **41**, 477 (1919).

[5] Briggs: J. Phys. Chem., **9**, 617 (1905).

[6] D'Huart and Hackspill: Compt. rend., **180**, 1581 (1925).

[7] McHaffie and Lenher: J. Chem. Soc., **127**, 1559 (1925); **1926**, 1785; Lenher: **1927**, 272.

The acceptance of such a theory however placed us in direct opposition to the multimolecular theory of Eucken-Polyani. In other words we were forced to choose between the capillary or the multimolecular theories of adsorption. Such a position led to a careful examination of the experimental proofs of the existence of an adsorbed film of multimolecular dimensions.

Practically all of the evidence proving the existence of multimolecular adsorbed films was based on experiments made on glass. This material while admirably suitable for obtaining optically plane surfaces seemed to us to offer the possibility of easily being roughened from the standpoint of molecular dimensions. Glass is not a chemically inert substance, it being admittedly attacked by water and acids. The results of such action must be the elimination of alkali and the deposition on the surface of amorphous silica. It therefore seemed plausible to seriously question the results of all adsorption measurements made on acid-cleaned glass surfaces in so far as the results were interpreted from the standpoint of molecularly plane surfaces.

While it is true that most of the measurements were made on glass surfaces, a number of other surfaces were also employed, such as mica, platinum, and quartz. The present paper does not deal experimentally with any of the latter surfaces; but it is pertinent to the discussion that follows to point out the possibility of all of these surfaces being not plane from the molecular dimensions standpoint. Mica surely exhibits capillary spaces between its lamellae, platinum is roughened by alternate heating and cooling (the so-called "activation" of its surface). Furthermore highly polished platinum in X-ray diffraction studies no longer shows the characteristic platinum lines, but exhibits the structure of an amorphous substance. Quartz when heated to the melting point is known to sublime, which fact may easily account for the failure to obtain molecularly plane surfaces with this material.

We were led to believe that a supercooled liquid offered the best possibility of securing a plane surface. The surface energy of the liquid would insure a minimum surface, and if care were exercised to prevent corrosion of this surface after cooling it should be plane.

The adsorption measurements were made according to the method of McHaffie and Lenher, this being considered as offering the fewest experimental difficulties.

The method employed by McHaffie and Lenher in studying the thickness of adsorbed films was to measure the vapor pressure in a vessel of known volume and surface area throughout a temperature range sufficient to insure the existence at the lower temperature of liquid and at the higher temperature of all the vapor in the gaseous condition. When no adsorption of the vapor on the walls of the vessel took place, the P. T. diagram would appear as in Fig. 1, curve A, O, C.

The straight line (CB, O) represents the ordinary thermal increase of gaseous pressure with increasing temperature, while the lower curve (A, O) is the vapor pressure curve of the condensed vapor. If however the vapor is appreciably adsorbed the curve (B, C) will no longer intersect the vapor pressure curve (A, O) at the point (O) but will follow a course as shown by

the dotted line. It is further evident that one may calculate the total number of molecules of water vapor present at the point c, this number should remain constant at all temperatures above T°, i.e. above the dew point. It is obvious however that the total number of molecules has decreased at points along the dotted curve and that this decrease may be simply calculated and thus the number of molecules adsorbed be ascertained.

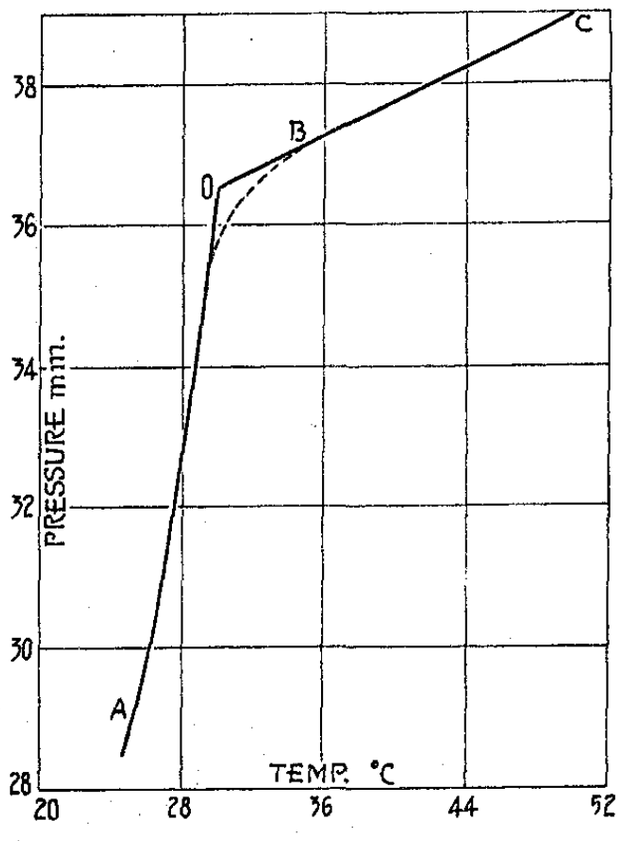


FIG. 1

As stated above the results of McHaffie and Lenher showed marked adsorption i.e. marked deviation from the ideal P. T. curve (I). In fact the thickness of the adsorbed water film on glass was found to be of the order of a hundred molecules, on platinum, and quartz thinner layers were found, but still decidedly multimolecular in thickness.

The weak point in the work was the assumption that glass cleaned with chromic and nitric acids still presents a plane surface. The present writers were strongly of the opinion that such a cleaning dissolved out some of the alkali from the glass, leaving a roughened surface of unknown extent, and in addition left the silica in an amorphous state which is most suitably adapted for the adsorption of vapors. We therefore determined to repeat these measurements taking special precautions to obtain a truly plane surface. At this point it may be of interest to make a rough calculation of the amount of amorphous silica that would be sufficient to account for the total adsorption in the case of toluene. Subsequent results will show that the maximum adsorption of toluene at the saturation pressure amounted to .000075 gm., to

adsorb this amount of toluene only .2 mgm. of silica gel is required. It is therefore entirely probable that by the action of strong acids on glass this small amount of amorphous silica may well be produced. From this calculation it is evident that it is impossible to believe that the surface of acid-washed glass presents a plane surface. However a freshly molten glass surface that had come in contact only with dry air should present a truly plane surface

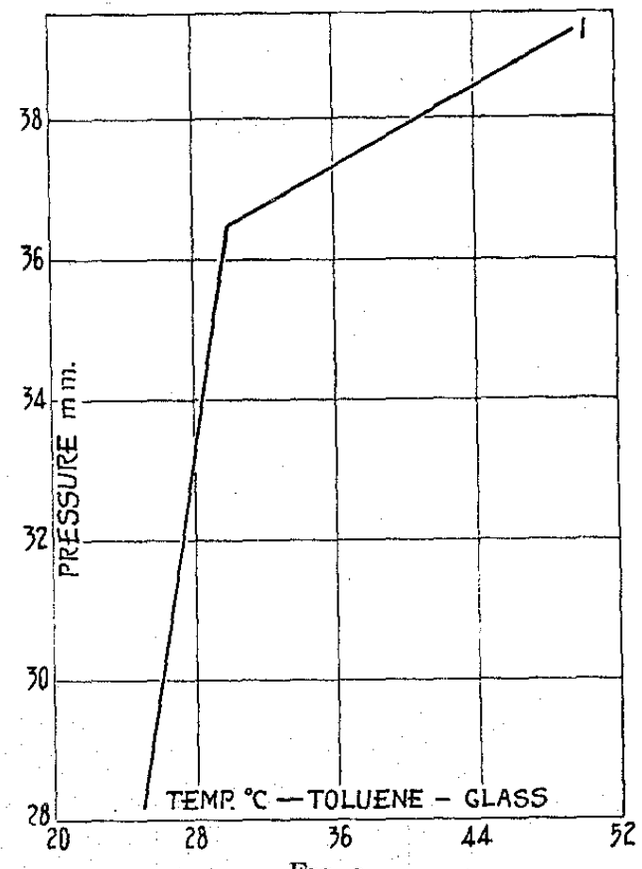


FIG. 2

from the standpoint of adsorption measurements. Accordingly a glass bulb was blown, the glass blower blowing through P_2O_5 during the operation. Furthermore in order to avoid any possible solvent action of water upon the glass surface it was decided to study the adsorption of toluene.

While it is true that McHaffie and Lenher obtained adsorption when working with water vapor on quartz and platinum surfaces, it is significant that the "thickness" of the layers on these surfaces was much less than on etched glass. The quartz was washed with acid and it is highly probable that a roughening took place during the operation. Platinum is known to be activated by heating in air, this we believe is due to the formation of finely divided platinum on its surface.

The apparatus is essentially the same as that employed by McHaffie and Lenher. The temperatures were carefully measured and the pressures read with a cathetometer to within .03 mm. The results obtained with toluene vapor on a virgin glass surface are given in Tables I and II and these same data are graphically shown in Curves (2) and (1). It can be immediately seen that toluene vapor shows no adsorption at any temperature. It is to be

noted that the method is not sufficiently sensitive to ascertain the presence of a unimolecular layer. Such a layer may be and undoubtedly is present at all temperatures. But we may definitely draw the most important conclusion from this experiment, that a multi-molecular layer film of toluene cannot xist on a plane surface.

In order to further prove our contention that a glass surface treated with cleaning solution and with nitric acid is no longer plane, we cleaned a bulb with the above acids, washed and thoroughly dried the surface. This bulb was then sealed to our apparatus and another series of P. T. measurements made with toluene vapor. The results are tabulated in Table III and graphically shown in Curve (3) Fig. 2.

TABLE I

Virgin Glass Surface.		Toluene.	
T °C.	P Mm.	T °C.	P Mm.
50.00	39.25	30.80	36.60
47.00	38.90	31.00	36.60
45.00	38.65	30.00	36.30
43.50	38.40	29.71	35.70
40.00	37.90	29.40	35.30
37.00	37.65	29.20	34.90
35.00	37.35	29.00	34.50
33.00	36.95	28.00	32.85
30.07	36.45	27.04	31.25
30.60	36.55	26.00	29.80
30.40	36.55	25.06	28.15
30.20	36.50	25.80	29.35

TABLE II

Virgin Glass Surface.		Toluene.	
T °C.	P Mm.	T °C.	P Mm.
50.00	30.95	26.04	28.65
47.00	30.70	25.80	28.60
45.00	30.60	25.60	28.55
40.00	30.00	25.45	28.55
43.00	30.35	25.20	28.20
37.10	29.70	25.00	28.00
35.00	29.55	24.80	27.65
33.00	29.35	24.40	27.15
31.00	29.20	24.00	26.70
30.04	29.05	23.00	25.20
29.00	28.95	22.00	23.85
28.07	28.85	21.00	22.65
27.07	28.75	20.00	21.60

TABLE III

Acid-treated Glass Surface.		Toluene.	
T °C.	P Mm.	T °C.	P Mm.
50.00	30.40	28.80	28.23
47.05	30.10	29.15	28.30
43.50	29.85	27.81	28.10
40.00	29.45	27.00	27.93
38.00	29.25	26.00	27.75
35.10	29.00	25.00	27.55
33.12	28.75	24.60	27.20
32.20	28.60	23.20	25.80
30.00	28.35	22.20	24.25

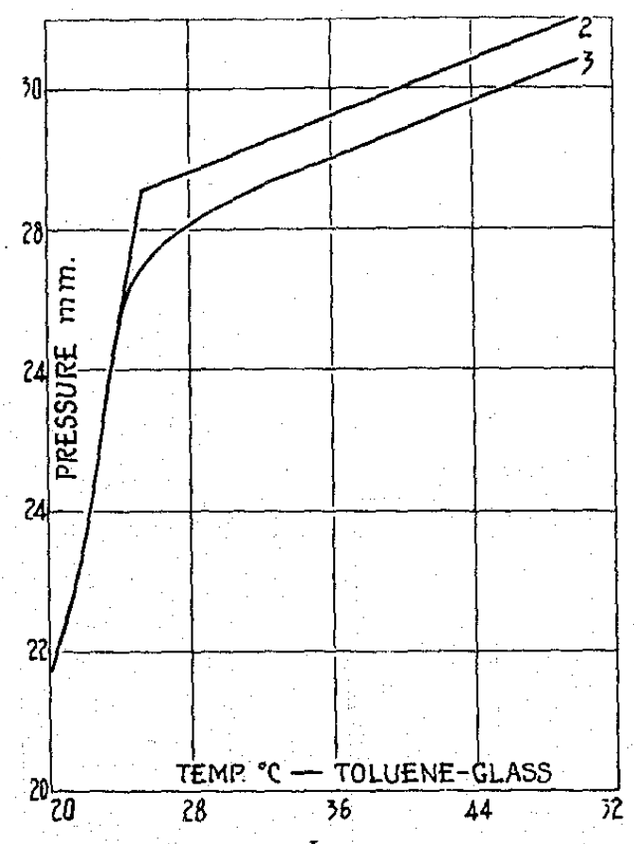


FIG. 3

It is to be noted that in the case of the acid-washed surface very different results were obtained from those on the virgin glass surface. In the former case we duplicated the experiments of McHaffie and Lenher made with water vapor. There is a decided rounding of the flex point of the curve which undoubtedly is due to the removal of the toluene from the vapor phase before the condensation temperature is reached. In other words adsorption of the toluene vapor occurs on the glass surface. But it is surely absurd to attempt to calculate the thickness of this adsorbed layer, for we have absolutely no information regarding the extent of the surface. This adsorption undoubtedly

owes its origin to the capillary condensation of the toluene vapor in the amorphous silica produced by the action of water and acid on the glass surface.

Experiments were also carried out with water vapor on virgin glass surfaces. The results of such measurements are given in Tables IV-VI and curves (4, 5, 6), Fig. 3.

TABLE IV

Virgin Glass Surface.		Water.	
T °C.	P Mm.	T °C.	P Mm.
50.00	24.00	30.00	22.00
47.00	23.70	29.90	21.90
45.00	23.50	29.70	21.70
43.00	23.35	29.50	21.55
40.00	23.05	29.00	21.35
37.00	22.75	28.00	20.65
35.00	22.50	27.50	20.50
33.15	22.35	26.00	19.85
32.50	22.25	25.00	19.20
31.00	22.10		

TABLE V

Water-etched Glass Surface.		Water.	
T °C.	P Mm.	T °C.	P Mm.
25.09	19.10	31.40	21.75
26.00	19.55	32.37	21.90
27.00	19.85	33.88	22.20
28.14	20.25	35.00	22.25
28.70	20.70	37.00	22.45
29.00	21.05	40.00	22.70
29.50	21.30	42.90	23.05
29.74	21.40	45.00	23.20
30.00	21.35	50.00	23.55
30.49	21.55		

TABLE VI

Water-etched Glass Surface.		Water.	
T °C.	P Mm.	T °C.	P Mm.
25.07	18.70	30.44	20.70
27.10	19.25	32.03	20.95
28.04	19.70	35.07	21.45
29.10	20.00	38.40	22.10
29.42	20.25	42.65	22.60
29.90	20.45	45.00	22.80

A number of interesting points in connection with these experiments are to be noted. In curve (4) Fig. 3, which represents measurements made with water vapor on a virgin glass surface, care being exercised that in the filling of the bulb with vapor no condensation was allowed to take place. Apparently these results show no adsorption of the water vapor. However the intersection of the two curves does not occur on the vapor pressure curve of water, i.e. the lower portion of the curve indicates a decided lowering of the water pressure. Such a result would be expected if the water dissolved some of the soluble constituents of the glass, such as sodium hydroxide. Curve (5)

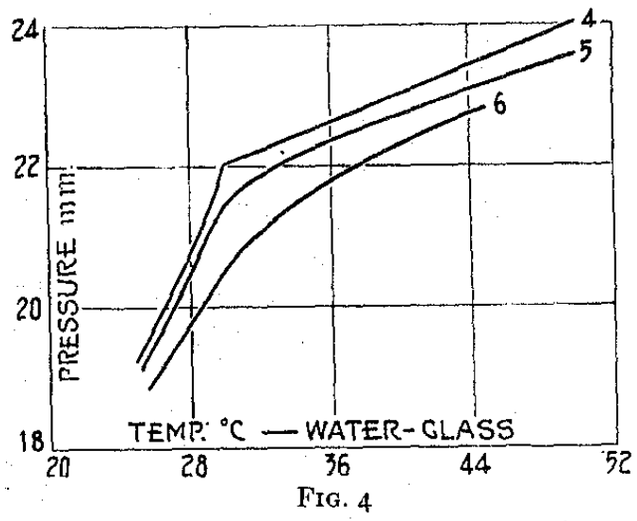


FIG. 4

and Table V show the results obtained when measurements were taken in the reverse direction, i.e. when the temperatures were increased and the corresponding pressures measured. Here we have marked evidence of "adsorption" having taken place. But inasmuch as we do not know how much the vapor pressure is reduced by the solutes present, or by the capillary action of the amorphous silica, it is absurd to attempt a calculation as to molecular thickness of the adsorbed film, etc. Curve (6) and Table VI show that as time goes on the solvent action of the water vapor on the glass increases i.e. there is now a most marked divergence of the P. T. curve from the ideal case where no adsorption takes place. At this point it is interesting to note that a fresh glass bulb was filled with water vapor and allowed to stand for four months. At the end of this time only a vapor pressure curve was obtained on making the P. T. measurements. This indicated that the action proceeded until a saturated solution was present on the glass surface.

Of course these observations are extreme, due to the fact that a fresh glass surface was employed. Practically all investigators when dealing with glass have washed the surface either with water or with acids. This of course tends to remove the soluble alkali, leaving the residue of amorphous silica nevertheless.

In order to further verify our conclusions regarding the action of water on fresh glass surfaces, we added a few cc. of water to one of our freshly blown

bulbs together with phenolphthalein as an indicator. A distinct alkaline reaction was obtained, in fact we were able to titrate with dilute acid and thus roughly ascertain the amount of alkali dissolved from the glass.

The importance of the above work is truly great provided we are justified in drawing general conclusions from the toluene experiments. There is little information regarding adsorption phenomena that can be gained from the water experiments. We have shown that water vapor attacks fresh glass surfaces in a manner sufficient to destroy the planeness of the surface and thus render all adsorption measurements on such surfaces vague and meaningless. In the case of toluene vapor however there is evidently no action on the glass, the surface remains plane, and important conclusions regarding the thickness of the adsorbed film may be drawn. Whether or not the results obtained with toluene are equally true with other vapors on other plane surfaces is impossible at present to say. We are planning to investigate the adsorption of vapors of polar compounds on plane glass surfaces, and also to attempt to obtain a plane surface which will permit the measurement of the adsorption of water vapor.

If such studies verify our present belief, namely, that the adsorbed vapor film is unimolecular in thickness even at the saturation pressure, then a most important step in the theory of adsorption will have been taken. Such an experimentally proven fact would immediately render untenable the theories of adsorption proposed by Eucken and Polyani. The very essence of such theories is that the adsorbed layer is multimolecular in thickness and they must necessarily be abandoned if it can be proven that the layer is never greater than unimolecular in thickness on a plane surface.

There remain the Langmuirian theory for plane surfaces, and the capillary theory to account for the adsorption by highly porous bodies.

Summary

1. It has been shown that the thickness of the adsorbed film of toluene on a plane surface is never greater than unimolecular, even at saturation pressures.

2. Glass washed with acids and water does not present a plane surface.

3. Water vapor reacts with fresh glass surfaces so as to render the latter no longer plane.

4. The significance of the above experiments was briefly discussed in relation to their bearing on the existing theories of adsorption.

Baltimore, Md.

QC 95 - 112

THE PHOTOGRAPHIC EMULSION. I. THE COMPARISON OF EMULSIONS MADE WITH DIFFERENT BROMIDES*

BY BURT H. CARROLL AND DONALD HUBBARD

Introduction

The recent rapid progress of photographic science has been largely through study of completed materials, and there can be little doubt of the value of studying photographic sensitivity from the standpoint of the conditions under which it originates—a subject which, for commercial reasons, has been almost entirely a secret for a generation. The Bureau of Standards has accordingly undertaken an investigation of fundamental factors in emulsion making.[1] While much of the material presented here may be common knowledge to emulsion makers, it has never been published in quantitative form, and it is a fact that the literature, and also the verbal opinions which the writers have been able to obtain from various sources, are both filled with contradictions regarding the most elementary points of emulsion making. These contradictions probably arise from the widely varying conditions under which emulsions may be made and the rapid variations in the influence of any given factor as the type of emulsion is changed. Though the problem of securing systematic knowledge of the subject is in many quarters considered hopeless of solution, and though indirect methods have accomplished much, we believe in the possibilities of a frontal attack, provided that all information of possible significance be reported.

As a means of outlining the variables which need to be studied, a very brief description of emulsion making will be given. So far as we know, the only process to be considered for fast emulsions is the addition of a silver salt solution, either neutral or ammoniacal, to a solution of bromide or mixed bromide and iodide containing gelatin. The bromide is invariably in excess. The known variables in this first and most important step are numerous. Enumerating them without specifying their particular importance, they are: the other ions of the silver and halogen compounds; the absolute concentrations; the relative excess bromide; the relative percentage of iodide; the temperature; the method and rate of mixing; the hydrogen ion concentration (pH); the presence of ammonia; the quality of gelatin.[2] After mixing (or "emulsification") the emulsion is commonly "ripened" for a time by digestion

* Published by Permission of the Director of the National Bureau of Standards of the U. S. Department of Commerce.

[1] The investigation was originally carried on by Dr. F. M. Walters, now of the Carnegie Institute of Technology, and the senior author. The equipment of the laboratory, and development of much of our present technique of emulsion making, date from this period and the data on emulsions 6-4 and 6-5, quoted in this paper, were obtained while Dr. Walters was associated with the project.

[2] Assuming for the gelatin good physical properties and the absence of such impurities as salts of heavy metals and reducing agents, the concentration of sensitizers such as thiocarbamides appears to be the major factor in determining its photographic quality.

in the presence of the excess bromide and the by-products of the reaction; more gelatin is commonly added towards the end of the ripening. Ammonia is introduced at some point into almost all fast emulsions; in this country at least, more frequently during the ripening of an emulsion mixed in neutral solution than in the silver solution. Many other materials have been added to emulsions; citric acid and alcohol are frequently mentioned.

The most important variables in the ripening process appear to be the temperature and concentrations with special reference to soluble bromide and ammonia; the extent to which ripening can profitably be carried is controlled by the original conditions of emulsification.

Having obtained the desired degree of ripening, the usual practice is to chill the emulsion to a firm jelly, then shred, and wash in cold water to remove soluble salts. The pH and dissolved salts in the wash water have considerable influence by their effect on the swelling. An alternative procedure, which we have found useful in experimental work, is to centrifuge the silver halide out and re-emulsify in pure gelatin solution. After washing, the emulsion is remelted, commonly with the addition of more gelatin, and usually digested for some time at a moderate temperature. This step is omitted in the old emulsion formulae found in the literature; in fact it is usually recommended to melt with the minimum possible heating. The apparent variables in this step are temperature, pH[1] and the amount of gelatin added after melting. Before coating, chrome alum in quantities said to be photographically inert, is commonly added to harden the gelatin. Addition of small amounts of soluble bromide is recommended in the old formulae. Sensitizing dyes, with the exception of the eosins, which may be introduced into the original mix, are always added after washing. The concentration of dye and of soluble bromide are of considerable importance as well as the individual characteristics of the dye.

The Comparison of Emulsions made with Different Bromides

Eder[2] states that only potassium and ammonium bromides are to be considered for emulsion making and our original program was limited to a comparison of these two salts. Having detected differences between emulsions made with them, the experiments were extended to include sodium, calcium, cadmium, and zinc bromides.

Lüppo-Cramer[3] states as a result of his general experience that potassium bromide is better for some types of emulsions, and ammonium bromide for others. Eder suggests that because of its more acid reaction, the latter may give less fog in cooked emulsions. Lüppo-Cramer has published a recent paper on the ripening process[4], in which he notes the very fine grain and slow speed of a cooked emulsion made with $CdBr_2$; this he attributes to retardation of the ripening by formation of a double salt with the AgBr, but we are un-

[1] Rawlings and Glassett: Phot. J., **66**, 495 (1926).
[2] "Ausführliches Handbuch der Photographie," **3**, 19.
[3] Z. wiss. Phot., **23**, 290 (1925).
[4] Z. wiss. Phot., **24**, 291 (1926).

able to find any evidence for the existence of such a compound. He found sodium and potassium bromides to be equivalent. Lithium bromide caused faster ripening and more fog, while barium, strontium and magnesium bromides were approximately equivalent to potassium bromide. No quantitative data are given.

Eder and Pizzighelli[1] compared silver chloride-gelatin emulsions made with various chlorides, finding that the chlorides of the alkali metals gave faster and softer emulsions than those of the alkaline earths, while emulsions made with zinc and cadmium chlorides were very slow, clear and "hard".

Schweitzer[2] reports that infra-red sensitive emulsions may be made by the use of mixtures of NH_4Br and $ZnBr_2$, and the famous infra-red sensitive collodion emulsions of Abney[3] were made with $ZnBr_2$. These are probably cases of sensitization by colloidal silver, from the fog readily produced under these conditions.

Suggestions as to the mechanism of the differences between the bromides are even rarer than experimental results. Differences in solubility of the silver halide have been suggested by Lüppo-Cramer and by Eder. Slater-Price[4] postulates that adsorbed bromide may be built into the crystal lattice of the grain, introducing strains depending on the dimensions of the cation.

We believe the most probable mechanisms to be as follows; one or more of these being operative when a given change in cation is made:

1. Adsorption on the silver bromide grains, affecting the crystal habit and recrystallization; the ripening is normally controlled more by the rate of recrystallization than by the rate of solution.

2. Alteration of the pH by hydrolysis of the bromide or by repression of the dissociation of ammonia.

3. Alteration of the solubility of the silver bromide in the emulsion.

4. The removal of ammonia as complex cation, affecting solubility, pH, or crystal habit of the grain.

5. Changes in the viscosity and protective action of the gelatin.

In the following ammonia process formula, we have a type of emulsion in which a considerable amount of ripening from the standpoint of both speed and grain size, occurs after the mixing ("emulsification") is complete; in this case it may be possible to distinguish between effects on the formation of the grains and on the ripening. It is obviously impossible to precipitate crystals of the size and perfection characteristic of the grains of modern fast emulsion; they must be grown from their original ultramicroscopic beginnings. But we have evidence[5] that all the processes commonly associated with ripening go on

[1] "Ausführliches Handbuch der Photographie," 3, 919.

[2] Phot. Abs. 6, No. 408.

[3] Phil. Trans., **171** II, 655 (1880); **177** II, 547 (1886).

[4] Phot. J., 65, 303 (1925).

[5] For example, emulsions 6-4 and 6-5 were made with the proportions given later as the neutral formula, but with different gelatin. 6-4 was mixed comparatively rapidly (five minutes); initial speed 90, γ_6 0.92, average grain area 0.33μ^2; after 80 minutes ripening at 75°, the speed was 200, γ_3 0.77, average grain area 1.38μ^2. The mixing of 6-5 was extended over a period of forty minutes; speed directly after completion of mixing 230, γ_t 0.5[5], average grain area, 1.89μ^2, indicating much more ripening than 6-4 after 80 minutes.

at a greatly accelerated rate during the mixing, so that, as in the case of the following neutral formula, the grains may be well formed at the end of a gradual emulsification, and the emulsion is comparatively little changed by subsequent "ripening". Even with the ammonia process formula, the growth of grains and nuclei during mixing is far from negligible, and it will be difficult to say definitely that a given one of the factors just mentioned influences ripening or influences the formation of the grain.

1. Experimental

Materials.

The *alkali bromides* were commercial "c.p." salts free from heavy metal and iron, and contained less than one-half per cent chloride. NaBr, because of its variable water content was used in solution.

Calcium bromide was purified by treating the solution with H_2S, filtering, making barely acid with HBr, and removing H_2S by prolonged bubbling with filtered air. It was used in solution without recrystallization.

Cadmium bromide was freed from bromate by treatment with HBr, and recrystallized from water and alcohol.

Zinc bromide was prepared by saturating redistilled HBr with analyzed zinc, free from heavy metals and iron. The solution was used without recrystallization.

Silver nitrate was spectroscopically free from other heavy metals and iron, and contained 0.05 per cent material not precipitated by HCl.

Gelatin.—Emulsions were made from all the bromides with two makes of gelatin of different types: Koepf "3738 hard" and Nelson No. 1.

Water.—Distilled water was used throughout.

Ammoniacal Emulsion Formula:

The larger number of tests were made with an ammonia process formula, washing by centrifuge. The centrifuge was used primarily because of the possibility of following the ripening process in a single batch of emulsion, but also because it greatly improves the keeping qualities of ammoniacal emulsions.

The ammonia process formula was as follows:

A.	Water	125 cc.
	$AgNO_3$	0.1765 gram equivalent (30.0 gm.)
	NH_4OH	0.353 gram equivalent —(28-30 cc. concentrated ammonia solution)
B.	Water	250 cc.
	Gelatin	12.5 gm.
	Bromide	0.218 gm. equivalent (for example, 26.0 gm. KBr)
	KI	0.0015 gm. equivalent (0.25 gm.)

The ammonia necessary to redissolve the silver (two mols per mol $AgNO_3$) is found to be reproducible to one per cent. The excess halide is twenty-five per cent; assuming complete precipitation of the iodide, the mol fraction AgI is 0.0085 (1.06 per cent by weight).

The emulsion is mixed in conventional fashion. The gelatin is soaked in the bromide solution for 15-25 minutes at room temperature, then placed in a thermostat at 45° ± 0.5° and stirred about 15 minutes until the gelatin is dissolved and the solution is at thermostat temperature. A standard size Pyrex beaker (1.5 liter) and glass stirrer at 250 r.p.m. are used; the silver solution at 25°-30° is added from a separatory funnel in 2.5 minutes.

Within two minutes after the completion of mixing, one quarter of the emulsion is removed, the rest continuing to ripen at a constant temperature of 45°, with stirring. The sample is centrifuged at 3000 r.p.m. in a five-inch hard rubber bowl. The time required for separation of at least 95 per cent of the silver bromide varies from eight minutes with certain of the unripened emulsions to two minutes after long ripening. When separation is complete, the bowl is drained, the silver bromide re-suspended in 100 cc. of one per cent gelatin solution and the centrifuging repeated. Gelatin solution has been found preferable to water for washing, as when much of the gelatin is washed from the precipitate it no longer adheres properly to the walls of the bowl. Two separations have been found to give sufficient washing, the soluble bromide and ammonia being eliminated as completely as by ordinary washing. After the second separation, the silver bromide is suspended for coating in a solution of 12.5 gm. of gelatin in 175 cc. of water. After warming to 45°, it is filtered through an open (Whatman No. 41) paper and 10 cc. of 60 per cent alcohol is added to break foam and assist in setting.

Samples are again taken at approximately 30, 60, and 120 minutes from the end of the mix, and treated like the first. This gives four stages of ripening, from the practicable minimum to overripening. The progress of the ripening can be followed by the texture of the silver bromide on the wall of the centrifuge bowl, which becomes very distinctly rougher with each successive sample.

The plates are machine-coated, with 9-10 cc. emulsion per 100 cm^2. (4 mg. AgBr per cm^2.), a thickness which experiment has shown to be sufficient to eliminate the effect of coating thickness on gamma. They are dried at 17-19°C. The air after leaving the plates passes over ammonia coils which keep the humidity in the room at approximately 60 per cent.

Neutral Emulsion Formula:

The "cooked" emulsion formula which was used was much less satisfactory, but the results obtained with it were parallel with the others. The solutions were as follows:

A.	Water	225 cc.
	Gelatin (Koepf)	10 gm.
	Bromide	0.265 gm. equivalent (50% excess halide, for example, 31.5 gm. KBr)
	KI	0.0015 gm. equivalent (0.25 gm)
B.	Water	100 cc.
	$AgNO_3$	0.1765 gm. equivalent (30.0 gm)

The emulsion was mixed at 75°C, in the same apparatus, with the important exception that the silver nitrate solution was delivered from a capillary

stem funnel which increased the mixing time to 27 minutes, the idea being to secure a better range in grain size. Samples were taken 30, 60 and 105 minutes from the start of the mix. The results suggest that the grains first formed were over-ripened before the mixing was completed.

The emulsion was washed in the centrifuge and otherwise treated the same as the ammonia emulsion.

Methods of Testing:

The standard sensitometric methods of the Bureau were used. Backed test strips were given a non-intermittent sector wheel exposure at an intensity

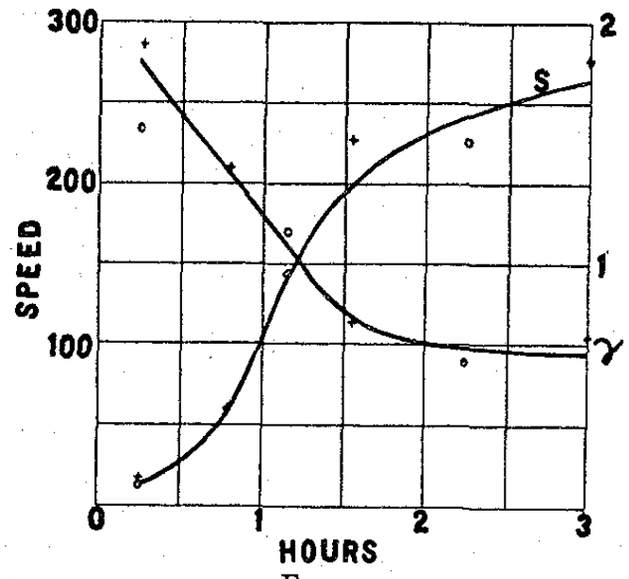


FIG. 1

of one candle meter, color temperature 5325°K; brush developed in unbromide dpyro-soda*, and densities measured in diffuse light with a Martens photometer. Fog densities are automatically subtracted by the photometer as used; with backed plates, the fog strip is uniform within the limits of error of development for the entire length.

The grain of all experimental emulsions was photographed at 1500 diameters, using a Bausch and Lomb 2 mm. apochromatic objective N. A. 1.3, and Zeiss Homal IV ocular. The illuminating system consists of a Point-o-lite lamp, condenser to give approximately a parallel beam, Wratten "C" filter, and aplanat substage condenser N. A. 1.4. Measurements of grain size were made from enlargements to 5000 diameters. Circles of the proper diameter have been found more convenient than linear rules. The size classes differed by $0.2\mu^2$.

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* Solutions:

A.		B.		C.	
Water	1000 cc.	Water	1000 cc.	Water	1000 cc.
Pyro	60 gm.	Na_2SO_3	95 gm.	Na_2CO_3 (c.p.)	70 gm.
$K_2S_2O_5$	12 gm.	(Actual Na_2SO_3 determined by analysis)			

1 part each A, B, and C to 7 of water; developed 3, 6, and 12 minutes at 20°C.

TABLE I. Ammonia Process Emulsions

Bromide	Emulsion Number	Ripening Time	Koepf Gelatin Speed	γ_3	γ_6	γ_{12}	Fog_3	Fog_6	Fog_{12}	Average Grain size μ^2	Emulsion Number	Ripening Time	Nelson Gelatin Speed	γ_3	γ_6	γ_{12}	Fog_3	Fog_6	Fog_{12}
NH Br	8–63–1	4 min	26	1.62	2.42	3.3	0.02	0.09	0.18	0.16	8–61–1	4 min	50	2.1	3.1	3.6	0.05	0.13	0.26
	2	31 "	160	0.88	1.50	2.22	.12	.20	.38	0.35	2	32 "	100	1.40	2.15	3.2	.12	.22	.41
	3	63 "	340	0.58	0.97	1.50	.09	.24	.56	0.99	3	62 "	190	0.95	1.47	——	.14	.26	.51
	4	125 "	450	0.53	0.89	1.44	.07	.26	.58	1.46	4	121 "	350	0.72	1.08	1.54	.21	.47	.65
KBr	8–64–1	4 "	35	1.26	1.93	2.63	0.02	0.07	0.13	0.16	8–62–1	4 "	67	1.28	2.46	3.3	0.04	0.11	0.26
	2	35 "	160	0.76	1.24	1.92	.11	.33	.68	0.87	2	31 "	590	0.65	1.01	1.51	.32	.56	1.00
	3	61 "	335	0.54	0.88	1.49	.09	.25	.42	1.05	3	61 "	780	0.61	0.98	1.51	.25	.55	1.10
	4	121 "	500	0.57	1.04	1.75	.07	.24	.49	1.40	4	121 "	950	0.62	0.94	1.29	.23	.48	0.92
NaBr	8–67–1	4 "	26	1.55	2.11	2.67	0.04	0.08	0.13		8–73–1	3 "	45	1.70	2.20	3.1	0.01	0.05	0.14
	2	33 "	370	0.57	0.97	1.35	.23	.35	.60		2	32 "	680	0.52	1.06	1.69	.15	.31	.68
	3	63 "	460	0.43	0.77	1.05	.22	.34	.54		3	63 "	790	0.62	0.95	1.45	.20	.37	.77
	4	121 "	430	0.74	0.97	1.63	.15	.33	.57		4	119 "	800	0.66	1.09	1.63	.14	.28	.59
$CaBr_2$	8–65–1	4 "	12	1.53	2.50	3.2	0.02	0.06	0.17	12	8–74–1	4 "	23	2.35	3.2	4.2	0.01	0.03	0.11
	2	33 "	35	2.13	2.88	3.6	.06	.15	.37	.25	2	31 "	68	1.78	2.56	3.2	.05	.09	.20
	3	62 "	57	1.90	2.37	3.4	.08	.17	.34	.33	3	61 "	85	1.59	2.63	3.4	.08	.15	.29
	4	112 "	105	1.15	1.65	2.56	.08	.13	.34	.40	4	120 "	110	1.36	2.16	2.90			
													575*	0.54	0.80	1.20	.13	.21	.45
$CdBr_2$	8–66–1	4 "	2	0.24	0.40	0.53	0 01	0.05	0.13	.11									
	2	39 "	37	0.38	0.54	1.00	0.16	0.41	1.12	1.20									
	3	78 "	63	0.38	0.54	1.00	0.35	0.75	1.34	1.84									
	4	122 "	90	0.30	0.47	——	0.49	0.96	1.73	1.54									
25% Br as CdBr, 75% as KBr	8–70–1	3 "	5	1.15	1.95	2.13	0.03	0.09	0.19	.12	8–75–1	4 "	12	1.60	2.10	2.40	0.08	0.13	0.20
	2	36 "	300	0.43	0.74	1.07	.18	.30	.46	.20	2	31 "	410	0.60	0.90	1.20	.27	.37	.62
	3	67 "	240	0.55	0.88	1.28	.21	.48	.77	.81	3	61 "	575	0.56	0.87	1.23	.22	.32	.57
	4	122 "	275	0.53	0.83	1.18	.16	.39	.67	1.17	4	121 "	715	0.44	0.66	1.00	.25	.51	80
10% Br as CdBr, 90% as KBr	8–68–1	4 "	10	1.50	2.00	2.52	0.03	0.06	0.14	.13									
	2	31 "	110	1.23	1.88	2.50	.09	.18	.37	.33									
	3	61 "	450	0.51	0.87	1.42	.15	.28	.55	.53									
	4	124 "	530	0.56	0.74	1.14	.18	.45	.76	.87									
25% Br as ZnBr, 75% as KBr	8–71–1	5 "	8	1.08	1.61	2.40	0.06	0.13	0.25	.15	8–76–1	4 "	21	1.73	2.44	2.96	0.09	0.15	0.36
	2	33 "	300	0.57	0.98	1.46	.16	.45	.74	.67	2	31 "	205	0.70	1.00	1.60	.26	.48	0.98
	3	61 "	155	0.53	0.84	1.26	.16	.43	.78	1.37	3	61 "	510	0.51	0.85	1.21	.28	.48	1.02
	4	118 "	150	0.45	0.79	1.04	.15	.45	.79	1.79	4	116 "	455	0.45	0.71	1.15	.35	.71	1.34

* The lower portion of this curve is effectively a second straight line, giving the speed and gammas indicated.

Reproducibility of Emulsions:

The parallel results from the emulsions made in the two different gelatins are perhaps the best proof that the effects observed are correctly attributed to the cation of the bromide in question. But direct tests of the reproducibility of our emulsions indicate that it approaches that of the sensitometric methods[1]. Fig. 1 gives the data on two emulsions made by the same formula, comparing speed and gamma at all stages of ripening; 8-33 was made by one of the writers, and 8-58 by the other, a year later. Similar results have been obtained in other cases.

TABLE II

Neutral Emulsions (all with Koepf Gelatin)

Emulsion	Ripening time from start of mix.	Speed	γ_3	γ_6	γ_{12}	Fog_3	Fog_6	Fog_{12}	Average grain size μ^2
6–15–1	30 min	130	0.82	0.84	1.57	0.13	0.42	.87	1.03
2	61 "	150	0.50	0.86	1.28	.24	.47	.93	1.65
NH_4Br									1.89
3	105 "	175	0.60	0.85	1.30	.19	.43	.83	
6– 8–1	33 "	225	0.68	0.96	1.40	.14	.41	.88	0.93
2	70 "	235	0.64	0.88	1.45	.13	.43	.87	1.15
KBr									
6–17–1	30 "	105	0.76	1.14	2.26	.17	.40	.71	1.06
2	60 "	110	0.64	1.00	2.08	.18	.42	.74	0.99
$CaBr_2$									
3	105 "	105	0.69	1.20	1.50	.21	.46	.74	1.67
6–16–1	30 "	15	0.78	1.34	2.18	.07	.18	.41	0.10
2	60 "	15	0.96	1.44	2.18	.05	.15	.29	0.12
$CdBr_2$									
3	105 "	18	1.31	2.06	3.3	.13	.29	.55	0.14

These results will be considered in detail after taking up the determination of conditions in the emulsion which might be expected to influence the photographic properties.

The centrifuged emulsions have an unusual tendency to increase in speed on storage, which introduces some uncertainty as to what is to be taken as the true value. The general question of ripening after washing will be taken up in a later communication. We may state with confidence, however, that

[1] We have so far had no experiences with inexplicable mutations such as the case given by Renwick: Phot. J., 61, 333 (1921).

the changes in the emulsions in question, while rapid for the first two to three months, become progressively slower, so that the changes between three and twelve months are a small fraction of those in the first three. The tests in all cases were made between eight and nine months after coating, so that the difference in age, between any emulsions compared, becomes negligible. This storage ripening may apparently be eliminated by the proper amount of digestion before coating, but the correct amount varies with the emulsion and it was very desirable to avoid introducing another variable. We should, perhaps, mention that the storage ripening is equally marked in neutral and ammoniacal emulsions, and is prevented rather than accelerated by the addition of soluble bromides before coating.

The sensitometric data are presented in Tables I and II. Average grain size of some of the emulsions is included.

Solubility of AgBr in the emulsion, and pH:

The solubility of the silver halide in the (unwashed) emulsion has already been mentioned as of possible influence on the precipitation and ripening. Other conditions being the same, an increase in solubility would, by von Weimarn's theory, decrease the initial velocity of crystallization and, therefore, increase the average grain size. It would also increase the velocity of the Ostwald ripening. The solubility of silver bromide was determined under conditions approaching those of the (unwashed) emulsion as closely as practicable. As the separation of silver bromide from the solution could not be made quantitative in the presence of the gelatin, this was necessarily omitted, as was also the iodide. The ammonia was placed in the bromide solution to reduce changes in solubility during precipitation, and the silver bromide precipitated as in making an emulsion, temperature, and concentrations except as above noted, being the same. The mixture was stirred for an hour and sampled, with filtration, by the method of Walton and Judd[1]. Dissolved silver bromide was determined by diluting the sample with twenty times its volume of dilute HNO_3, digesting over night, and weighing the precipitated AgBr in Gooch crucibles. The method was tested by adding a known small amount of nitrate, just sufficient to give a precipitate, to a sample of the ammoniacal bromide solution. 18.7 and 18.0 mg. AgBr were recovered from an amount corresponding to 18.8 mg.

The pH of the solution was also determined by thymol blue, thymolphthalein, alizarine yellow or tropaeolin O, comparing with glycocoll-NaOH or borax-boric acid buffer solutions, as recommended by Sörensen and Palitzsch respectively.

Solubilities in the ammoniacal emulsions are given in Table III. The density of the solutions was not determined but the (volume) normality of the AgBr would be 0.00031 ± 0.00002 in the first case (KBr). The solubility of AgBr in NH_3, N 0.93 at 15° is 16 mg. per 100 cc. and at 25°, 52 mg.; extrapolating, it would be at least 100 at 45°.

[1] J. Am. Chem. Soc., **33**, 1036 (1911).

TABLE III

Solubility of AgBr at 45° in solutions of the composition of unwashed ammonia emulsions: NH_3, 0.93N; soluble bromide, 0.108N; soluble nitrate, 0.465N.

Bromide	Milligrams AgBr per 100 grams solution	pH
KBr	5.4	11.8 ± 0.5
NH_4Br	6.7	9.7 ± 0.2
NaBr	9.1	11.8 ± 0.5
$CaBr_2$	6.5	11.8 ± 0.5
$CdBr_2$	1.9	9.4 ± 0.2
25% Br as $CdBr_2$ / 75% Br as KBr	6.4	10.3 ± 0.2
25% Br as $ZnBr_2$ / 75% Br as KBr	4.5	10.1 ± 0.2
NH_4Br—Pyridine, 1.4N	(0.6)	7.5 ± 0.2
NH_4Br—NH_3, 0.47N	2.5	9.4 ± 0.2

The solubility of the silver bromide in the ammonia is thus seen to be greatly reduced by the presence of soluble bromide. The equilibrium in these solutions is too complex for calculation, but may be briefly discussed. Assuming that the solubility product $[Ag^+] \times [Br^-]$ remains approximately constant, the silver ion concentration must be greatly reduced by N 0.1 bromide, both by mass action and possible formation of complex anions such as $AgBr_2^-$. The concentration of the complex cation Ag $(2NH_3)^+$, dependent on Ag^+ and NH_3 concentrations, must be correspondingly reduced. Thus the further complication of the complex cadmium-or zinc-ammonia cation produces comparatively little effect on the solubility.

When pyridine (3 mols per mol AgBr) was substituted for ammonia, the solubility was too low for measurement by this method. This was also the case for the completed neutral emulsions. It was possible, however, to secure satisfactory data on the solubility in plain bromide solutions simply by addition of $AgNO_3$ of appropriate concentration until a permanent precipitate was formed. N 0.1 or N 0.01 $AgNO_3$ was used, the volumes being from 1 to 7 cc., to 100 cc. of normal bromide solution, so that there was little dilution of the latter. It will be noted that these solubilities given in Table IV are higher than those in the completed ammonia emulsions. As the solubility of the AgBr varies roughly as the square of the soluble bromide concentration, it falls during the mixing of the neutral emulsion lower than it ever goes in the ammonia process.

TABLE IV

Solubility AgBr at 74° in normal solutions of bromides

Soluble Bromide	Normality AgBr	Soluble Bromide	Normality AgBr
KBr	0.0013	$CaBr_2$	0.00115
NH_4Br	0.0014	$ZnBr_2$	0.00068
NaBr	0.00095	$CdBr_2$	0.00024

Effect of the Halides on the Gelatin:

Any attempt to explain the behavior of the emulsions in this way meets with the usual difficulty of interpreting physical tests on gelatin. A determination of the effectiveness as a protective colloid is most likely what is wanted in this case, but no satisfactory method has been devised. Viscosity was chosen, as it could be determined under the conditions of emulsion making. Measurements were made on Koepf gelatin at 45°, with a burette consistometer.[1] Concentrations were the same as in an ammonia process emulsion. After soaking for twenty minutes at room temperature, the gelatin was dissolved by heating for twenty-five minutes at 60° and filtered through a loose plug of glass wool. The determination was started after ten minutes in the 45° thermostat and viscosity burette. After measuring the viscosity of a "neutral" sample (pH. 5.2-5.4) ammonia was added to the remaining solution and another determination made after fifteen minutes. A third was made after ninety minutes at 45° with the ammonia. The observed viscosities in centipoises, are given in Table V.

TABLE V

3.6% gelatin solutions at 45.0°. Bromide, N 0.62; NH_3, N 0.94.

Bromide	Neutral Viscosity	Viscosity with Ammonia After 15 min.	Viscosity with Ammonia After 90 min.	pH with NH_3
None	0.0186	0.0229	0.0204	11.5
KBr	0.0230	0.0214	0.0181	11.3
NH_4Br	0.0222	0.0210	0.0195	9.8
NaBr	0.0234	0.0221	0.0194	11.3
$CaBr_2$	0.0234	0.0197	0.0177	11.2
10% Br as $CdBr_2$, 90% as KBr	0.0197	0.0197	0.0175	11.3
25% Br as $CdBr_2$, 75% as KBr	0.0178	0.0199	———	11.0
25% Br as $ZnBr_2$, 75% as KBr	0.0185	0.0200	0.0191	10.4

It is obvious that the alkali bromides and calcium bromide all increase the viscosity to the same extent, within the limits of experimental error and that the addition of the ammonia in the presence of the alkali bromides differs little in its effect from that of the same volume of water. The decrease in viscosity with calcium bromide is more marked. The effect of the cadmium and zinc bromides is opposite to that of the others, the viscosity being reduced. The increase in viscosity on adding ammonia may be ascribed to the elimination of the cadmium or zinc ion by formation of the ammonia complex. The rate of decrease in viscosity on long digestion of the mixtures increases with pH; no other influence can be detected.

[1] Herschel and Bulkley: Ind. Eng. Chem., **19**, 134 (1927).

It appears to be impossible to explain the differences between the emulsions in terms of the effects of the gelatin. The calcium and cadmium bromides alike give lower viscosities in the presence of the ammonia than do the alkali bromides, but the properties of the emulsions made with them differ in opposite directions from those made with alkali bromide.

Crystal Habit of Grains:

One point of interest, which the writers have never seen explicitly mentioned, is the influence of materials present in the original mix, on the crystal habit of the silver halide grains. This is illustrated by the photomicrographs

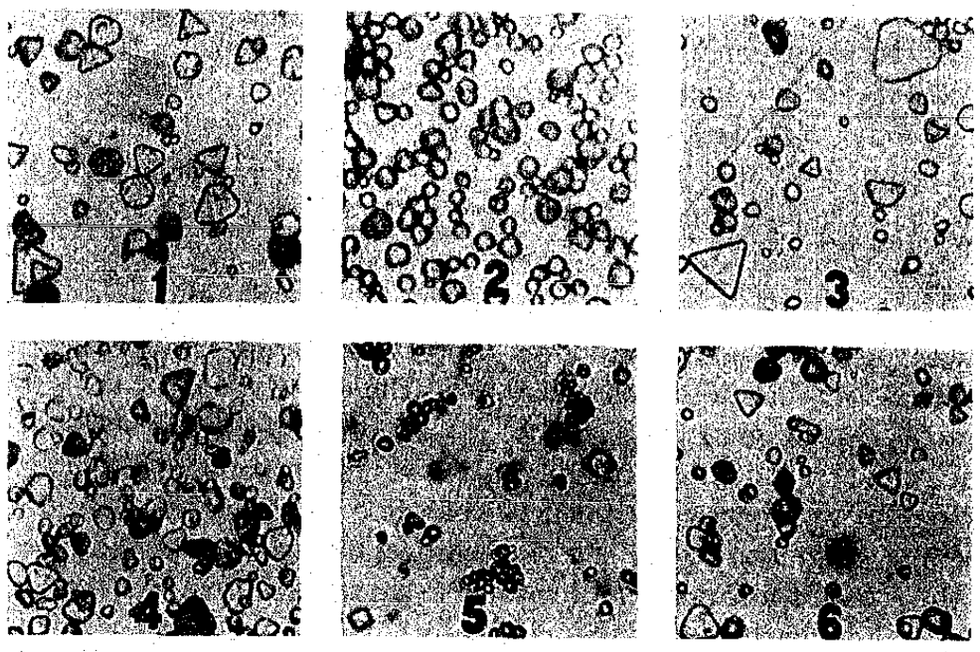


FIG. 2

Crystal habit of grains from emulsions made by different processes.
(1) Grains from neutral emulsion, made by mixing silver nitrate with mixed bromide-iodide solutions. (2) Ammonia in mix. (3) Ammonia and cadmium salts in mix. (4) Potassium cyanidein mix. (5) Pyridine in mix. (6) Diethylamine in mix. All at 3000 diameters.

of Fig. 2. When an ammoniacal mix is used, the ammonia being in either the silver or bromide solutions, the grains take a characteristic rounded form instead of the flat plates typical of the neutral emulsions. The spherical appearance of the grains is more apparent than real; it is largely due to their greater thickness and the very limited depth of focus of a high power microscope objective. On careful visual focussing, sharp angles, successively appear on one side or the other of the grain, but the whole grain can never be sharply focussed at once. As the ripening goes on, the grains become more distinctly hexagonal or triangular in shape, but the general shape is very persistent. The use of ammonia for ripening of emulsions mixed without it has no tendency to produce this form.

When cadmium or zinc was used in ammoniacal emulsions, the removal of the ammonia as complex cation caused the silver bromide grains to take the characteristic form of neutral emulsions. The influence of the ammonia

on the crystal habit of the silver bromide is apparently due to complex formation. It is not due to the alkalinity, since the addition of NaOH to emulsions to give the same pH as "full ammonia" had no influence on the habit of the grains; neither is it due to increased solubility, since emulsions made with KCN had flat hexagonal grains. Substitution of pyridine for ammonia gave fine grains with a strong tendency to coagulate, behaving somewhat like silver bromide without a protective colloid, so that it was difficult to secure a photomicrograph. The thickness of the grains is of the same order as their other dimensions; the larger ones are apparently tetrahedral. Diethylamine, on the other hand, gave flat plates, so the rounded grains are not characteristic of all nitrogen bases.

Under the same conditions of solubility and temperature, the flat plates would be expected to increase in area faster than the rounded grains, since the same change in mass produces a larger change in area, and since their shape is presumably due to more rapid growth at the edges. This is fulfilled in the case of the ammoniacal emulsions containing cadmium or zinc.

2. General Discussion

The left-hand set of curves in Fig. 3 (Emulsion 8-64) illustrate very well the general behavior of the ammonia process emulsions. The characteristic curve for the six-minute development, and the distribution of the projected area among the different class sizes of grains, are plotted on the same sheet. The unripened emulsion has a small grain and high gamma, but there is much more "toe" to the characteristic curve than in a good contrast emulsion. As the ripening progresses, there is a marked decrease in gamma and increase in speed; the straight line portion of the curve shortens more and more from the region of higher densities, and there is finally a decrease in speed. The average grain size steadily increases. The size-area curve broadens and flattens, so that the decrease in gamma is to be expected. One would, however, expect an increase in scale, which is not found, because the density for long exposures actually falls off with longer ripening. Part of this is due to the excessive fog on ripening for the longer times, but when the characteristic curves are plotted with fog included, there is still a marked loss of density at values of E greater than one c. m. s. This effect would be explained if there were a change with ripening in the photometric constant of the developed image. We have as yet no experimental evidence on this point. The other alternative is that a considerable portion of the grains have become undevelopable. The work of Svedberg, Schunk, and Anderson[1] indicates that in an emulsion with wide range of grain sensitivity, some of the more sensitive grains are solarized before the least sensitive are developable, but the percentage is too small to account for the results here. Furthermore, this loss of density never occurs when the emulsion is increased in sensitivity without change in grain size, by digestion after washing, or by storage. The preliminary results reported by Sheppard[2] show that variations in the photometric "constant" may be much

[1] Phot. J., **64**, 272 (1924).
[2] Phot. J., **66**, 470 (1926).

larger than had previously been reported. Assuming that the developed grains of the ripened and unripened emulsions have very roughly the same proportions, the larger grains should give the lower density, since the

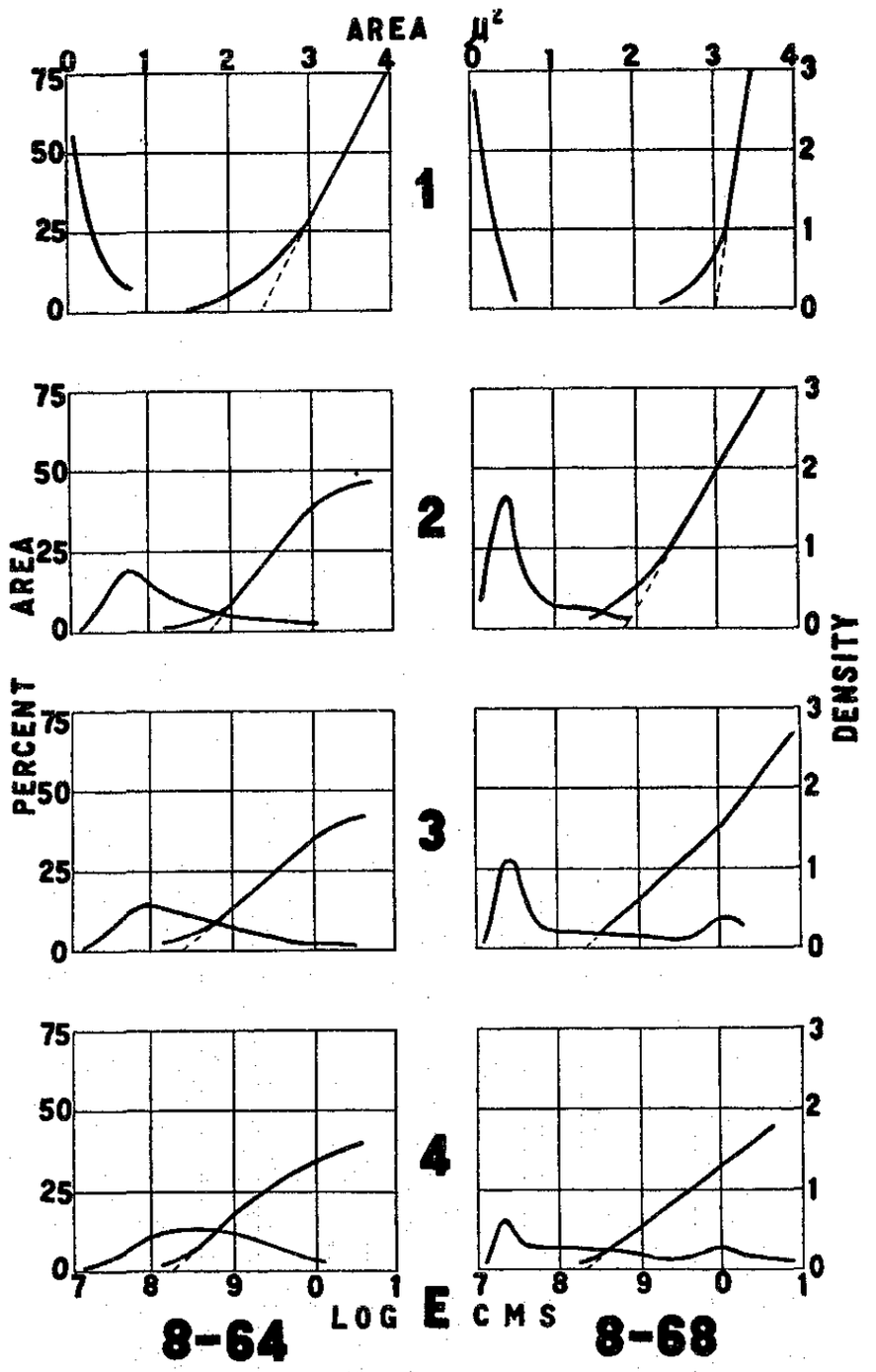


FIG. 3
Characteristic curve (for six-minute development) and distribution of total projected area between grains of different size classes, for two ammonia-process emulsions at four stages of ripening. 8-64 made with KBr, 8-68 with a mixture of KBr and CdBr₂.

same mass of silver would have a smaller projected area, and the minimum thickness of metal encountered in a developed grain is completely opaque to visible light.

The emulsions made with Nelson gelatin invariably show more speed and generally worse fog than those made with Koepf, and the difference appears

in the unripened stage; the former always have not only higher speed but higher gamma. Our experience in comparing different makes of gelatin in the same formula confirms the general rule that potential speed is always evident in the unripened state. This cannot be applied too freely in comparing the emulsions made with different bromides, since the ripening may proceed so differently.

Comparing the emulsions made with the alkali bromides, we find no certain differences between the sodium and potassium salts. The ripening of 8-61 with NH_4Br and Nelson gelatin is much slower than that of the corresponding 8-62 and 8-73, and 6-15 is slower than 6-8, but the differences between 8-63, 8-64, and 8-67, are within the limits of error. The pH of the ammoniacal emulsions containing NH_4Br is lower by 1.5 unit (Table V) than those with KBr, owing to repression of the dissociation of NH_4OH by mass action of the NH_4 ion. The other conditions being almost identical, this should be sufficient to account for the difference in rate of ripening.

The emulsions made with calcium bromide are consistently slower and cleaner. The difference is less marked in the case of the neutral emulsion (6-17), which, as would be expected from the solubility, has a grain size about the same as that of the corresponding emulsions made with ammonium and potassium bromides. The very slow ripening of the ammoniacal emulsions (8-65 and 8-74) we can explain only by adsorption of $Ca(OH)_2$ on the grains. The pH of these is close to that of saturated $Ca(OH)_2$ solution, and the turbidity of the viscosity samples was distinctly higher as determined by nephelometry, than that of the other bromides. As the ammonia was added with the silver solution, there might be momentary precipitation of $Ca(OH)_2$, and if this were adsorbed, the growth of the grain would certainly be retarded, and probably reaction with thiocarbamides as well. The photographic difference in the neutral emulsions is not to be explained in this way, however, and we are obliged to admit that there is a specific difference in behavior, still to be explained.

The emulsions containing cadmium or zinc bromide have a very fine grain in the unripened state. Even in the case of the ammonia process emulsions, the precipitation begins in the practically neutral bromide solution, the ammonia being added with the silver. The solubility of the silver halide in the bromide solution is, therefore one of the factors determining grain size. By von Weimarn's theory, the grain should be smaller because of the lesser solubility in cadmium or zinc bromide. The neutral emulsion with cadmium bromide remained very fine-grained and slow, the low solubility resulting in slow ripening. The ripening of the ammoniacal emulsions was much affected by the change in crystal habit of the grains, the flat plates being formed under conditions of comparatively high solubility with consequent very rapid change in area. The ripening becomes progressively more rapid with increasing proportions of cadmium in the series 8-68, 8-70, and 8-66. The great difference between the conditions under which the first and the last of the silver bromide is precipitated, in these emulsions, resulted in a peculiar distribution of grain size. Even the unripened emulsions contained some rather

large grains, and 8-68-2, 3, and 4 (Fig. 3) show a distinct secondary "hump" in the size-frequency curve. Corresponding to this wide range in grain size, there is a scale extraordinarily long for these emulsions with their rapid mix and long ripening. All the ammonia emulsions with zinc and cadmium bromide show in an exaggerated way, the mechanism of ripening which we believe is generally characteristic of the formation of a fast emulsion. However, when the mixing is retarded, so that most of the ripening takes place by the time the addition of the silver is completed, great differences are introduced by the continual supply of freshly precipitated silver bromide. Referring to Fig. 3 the unripened 8-68-1 has a rather pronounced "toe" to its characteristic curve. After 30 minutes ripening, 8-68-2, the toe extends to higher densities, accompanied by a general displacement of the curve to the left. After sixty minutes, 8-68-3, the toe has continued its development to become a second straight line, encroaching still further on the original straight line portion of the characteristic curve, and finally (8-68-4) absorbing it entirely. The presence of the large number of small grains still remaining prevents the loss of density at large exposures such as occurs in 8-64. The emulsions with cadmium, and even more with zinc were of little value because of the excessive fog characteristic even of the fresh plates; if this can be eliminated, these salts may have considerable value. Calcium bromide, on the other hand, may have possibilities for process emulsions.

The neutral emulsions have been given less consideration, having been over-ripened by too high temperature and too large an excess of bromide. The range of grain size which was the object of the slow mixing was actually obtained, but the expected scale did not materialize for the reasons just mentioned.

3. Summary

1. Emulsions of the rapid type have been prepared with potassium, ammonium, sodium, calcium, cadmium, and zinc bromides, or mixtures of the same, under otherwise identical conditions, and compared sensitometrically, and as to grain size.

2. Data on the solubility of silver bromide in the unwashed emulsions, on the pH and on the viscosity of gelatin in the presence of the different bromides, have been obtained for their bearing on the mechanism of emulsion making.

3. The observed differences between the emulsions can in most cases, be explained by simple chemical and physical principles.

ADSORPTION BY METALLIC HYDROXIDES. IV. ADSORPTION BY PRECIPITATED CHROMIUM HYDROXIDE

BY KSHITISH CHANDRA SEN

In the preceding papers, I have studied the adsorptive power of ferric hydroxide and aluminium hydroxide on acids. The results obtained with hydrated chromium oxide will now be given.

Hydrated chromium oxide has not been much studied as an adsorbent. There are only a few instances in the literature where this substance has been used in adsorption experiments. Thus Wöhler, Pluddemann and Wöhler[1] mention that chromium oxide adsorbs benzoic acid and acetic acid about equally; but practically no other instance can be found where chromium oxide has been used as an adsorbent for acids. Owing to this reason, the adsorptive power of this substance has been investigated in detail.

A peculiar fact in connection with hydrated chromium oxide is that, with this substance, no true equilibrium can be obtained, the amount of adsorption gradually increasing with time. But if the time of contact is kept constant, quite reproducible values of the amounts of adsorption can be obtained. Further the adsorption equilibrium is not a reversible one. These behaviours differentiate this substance from the hydrated oxides of iron and aluminium studied beforehand. In order therefore to get some comparative results, the same length of time (20 hours) as was given in the case of aluminium and iron hydroxides, has been given, and all other conditions have been kept the same.

Adsorption of Arsenious Acid

In the first instance, the adsorptive power of chromium hydroxide for arsenious acid will be given. Several samples of the hydroxide have been used, and it has been found that different samples give different values of adsorption. The hydroxide used in Table I was precipitated from chromium sulphate solution by means of excess of ammonia and freed from electrolytes partly by decantation and then by dialysis. On analysing the hydroxide after dialysis, it was however found to contain some sulphate, which could not be removed. The first experiment was made to test the reproducibility of the results.

TABLE I

Wt. of Cr_2O_3 = 0.5914 gr.; time = 20 hours; concentration and adsorption in cc I = N/18.302

Conc. As_2O_3	Adsorption	Conc. As_2O_3	Adsorption
191.5	155.5	114.9	107.9
191.5	155.5	114.9	107.9
153.2	135.2	76.6	74.6
153.2	135.2	76.6	74.6

[1] Z. physik. Chem., **62**, 664 (1908).

The above results show that when the time of contact is twenty hours, the amount of adsorption remains the same and quite reproducible results can be obtained in duplicate measurements. In Table II, the effect of time is shown.

TABLE II

Cr_2O_3 = 0.5914 gr.

Original conc. of As_2O_3 in grms.	Adsorption in 20 hours	Adsorption in 48 hours
0.5170	0.4198	0.4374

Cr_2O_3 = 0.3496 grm.

0.4556	0.2829	0.2991
0.2278	0.1954	0.2251

These results show that the time of contact has an important effect inasmuch as the amount of adsorption increases with the increase in the duration of contact. In Table III the adsorption of arsenious acid at different concentrations by a fixed amount of the hydroxide is shown.

TABLE III

Cr_2O_3 = 0.5914 gr.; volume = 100 cc.; KCl = 0.05 mole per litre.; time = 20 hours

Original conc. of As_2O_3 in grams	Conc. of solution after adsorption	Adsorption per gram adsorbent
0.5665	0.1206	0.7541
0.5170	0.09715	0.7099
0.4635	0.0648	0.6742
0.4136	0.0486	0.6172
0.3102	0.0175	0.4949
0.2068	0.0054	0.3405
0.1034	0.0008	0.1735

In Table IV, the effect of *varying the amount of the adsorbent* on the extent of adsorption from a constant amount of arsenious acid is shown.

TABLE IV

Conc. of As_2O_3 = 0.3102 gr.

A = amount of adsorbent in grams. B = concentration of solution after adsorption. C = adsorption per gram adsorbent.

A	B	C	A	B	C
0.1182	0.2052	0.8884	0.4728	0.0378	0.5762
0.2364	0.1256	0.7809	0.5914	0.0176	0.4949
0.3546	0.0729	0.6692	0.7092	0.0108	0.4223

Effect of volume when the total solute concentration is the same in all cases, Table V.

TABLE V

Conc. of As_2O_3 = 0.4136 grams; wt. of Cr_2O_3 = 0.5914 gr.

Volume of solution	Amount of adsorption	Volume of solution	Amount of adsorption
90 cc	0.3602	70 cc	0.3654
80 cc	0.3629	60 cc	0.3731

In the following tables, a smaller amount of the adsorbing material has been used. The object was primarily to compare the adsorption isotherms obtained by using different amounts of the adsorbent. The net amount of adsorption will thus be different. The results of adsorption experiments with varying amounts of As_2O_3 are shown in Table VI. Other conditions remain the same.

TABLE VI

Cr_2O_3 = 0.3496 gr.

A = original concentration of As_2O_3 in grams. B = concentration of solution after adsorption. C = adsorption per gram adsorbent.

A	B	C	A	B	C
0.5696	0.2631	0.8766	0.3417	0.0917	0.7150
0.4556	0.1726	0.8095	0.2848	0.0580	0.6486
0.3986	0.1322	0.7623	0.2278	0.0323	0.5591

Effect of volume when the total solute concentration is the same in each case, Table VII.

TABLE VII

Cr_2O_3 = 0.3496 gr.
Conc. of As_2O_3 = 0.2278 gr.

Volume of solution	Amount of adsorption	Volume of solution	Amount of adsorption
100 cc	0.1955	70 cc	0.2023
90 cc	0.1975	60 cc	0.2060
80 cc	0.2009		

Effect of volume when the total amount of solute is different but the concentration in terms of normality is the same in each case, Table VIII.

TABLE VIII

Cr_2O_3 = 0.3496 gr.
Conc. of As_2O_3 = 0.2278 gr. per 100 cc.

Volume of solution	Adsorption in grams	Volume of solution	Adsorption in grams
100 cc	0.19548	70 cc	0.15006
90 cc	0.18079	60 cc	0.131868
80 cc	0.16502		

Effect of temperature on the hydroxide. To study the effect of heat on the sample of chromium hydroxide, 0.3496 grams of the hydrated oxide was taken in flasks which were then immersed in boiling water for 15 minutes. The flasks were then cooled, and the adsorption values were measured in the usual way, Table IX.

TABLE IX

A = original concentration of As_2O_3 in grams. B = adsorption by oxide—not heated. C = adsorption by oxide—heated

A	B	C	A	B	C
0.39865	0.26649	0.23949	0.28475	0.2268	0.2138
0.3417	0.25002	0.22842	0.2278	0.19548	0.18738

It will be observed that the adsorptive power of the heated sample is much less than that of the sample which has not been heated.

In Table X the adsorption of sodium arsenite by the same sample of hydroxide is shown.

TABLE X

Cr_2O_3 = 0.3496 gr.

Concentration and adsorption in cc I_2 N/18.302

Conc. Na-arsenite	Amount adsorbed	Conc. Na-arsenite	Amount adsorbed
211.0	104.0	105.5	78.5
168.8	97.3	84.4	68.9
126.6	85.5		

In Table XI the relative adsorbability of sodium arsenite and arsenious acid when the initial concentration in iodine equivalents are the same, is compared.

TABLE XI

Cr_2O_3 = 0.3496 gr.

Concentration and adsorption in ccI_2 N/18.302

Original conc.	Adsorption of As_2O_3	Adsorption of Na-Arsenite	Original conc.	Adsorption of As_2O_3	Adsorption of Na-Arsenite
211.0	113.5	104.0	105.5	84.0	78.5
168.8	104.8	97.3	84.4	72.4	68.9
126.6	92.6	85.5			

It will be observed from Table XI that arsenious acid is more adsorbed than sodium arsenite. This result is therefore different from that obtained in the case of aluminium hydroxide where the amount of adsorption is the same in both cases.

The hydroxide which has been used so long, as has already been stated, contained appreciable amounts of sulphate which could not be freed from it by washing. It was therefore thought desirable to make some more experiments with a sample almost free from adsorbed impurities. Hence another

sample of chromium hydroxide was prepared from a chromic chloride solution with an excess of ammonia. This sample could be washed practically free from adsorbed chloride by continued dialysis. In Table XII some results on the adsorption of arsenious acid with this sample are given. Other conditions remain the same.

TABLE XII

Cr_2O_3 = 0.2610 gr.; time = 20 hours

A = original concentration of As_2O_3 in grams. B = concentration of solution after adsorption. C = adsorption per gram adsorbent

A	B	C	A	B	C
0.9350	0.7225	0.8141	0.4675	0.2788	0.7231
0.8415	0.6288	0.8149	0.3740	0.1975	0.6763
0.7480	0.5375	0.8065	0.2805	0.1200	0.6151
0.6545	0.4512	0.7789	0.1870	0.0488	0.5297
0.5610	0.3638	0.7556			

The effect of time on the amount of adsorption by this sample was also investigated, and the results are given in Table XIII.

TABLE XIII

Initial conc. of As_2O_3 = 0.1870 gr.

Time of contact	Adsorption in grams
20 hours	0.1382
40 "	0.1445
80 "	0.1532
120 "	0.1532

Initial conc. of As_2O_3 = 0.3740 gr

Time of contact	Adsorption in grams
20 hours	0.1765
40 "	0.1930
80 "	0.1980
120 "	0.2027
140 "	0.2040
160 "	0.2040

From these results it will be observed that with the increase in the time of contact, the adsorption also gradually increases and then reaches a maximum. The time required for reaching this maximum depends however on the initial concentration of the acid used. Since however a time interval of 20 hours was allowed in the cases of iron and aluminium hydroxides, the same length of time has been given in the case of chromium hydroxide also in order to obtain comparative results. This course was also desirable because the adsorption equilibrium in the case of chromic hydroxide is not reversible, whereas in the other two cases, it is reversible.

In Table XIV the adsorption of sodium arsenite by this sample of chromic hydroxide has also been investigated and compared to that of the pure arsenious acid.

TABLE XIV

Cr_2O_3 = 0.2610 gr.

Concentration and adsorption in ccI_2 N/19.72

Conc.	Adsorption of Na-arsenite	Adsorption of As_2O_3	Conc.	Adsorption of Na-arsenite	Adsorption of As_2O_3
224.0	74.0	78.9	112.2	59.2	64.2
187.0	71.0	75.0	74.8	47.8	55.8
149.6	66.1	70.6			

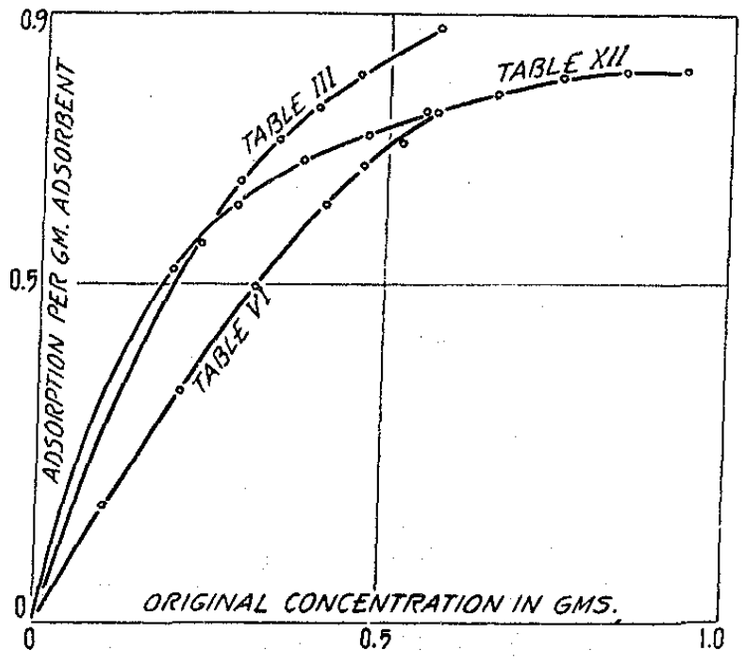


FIG. 1

Adsorption of arsenious acid by hydrous chromium oxides.

These results are quite similar to those given in Table XI and hence it is clear that hydrated chromic oxide adsorbs more of arsenious acid than sodium arsenite from equivalent concentrations when all the values are expressed in iodine equivalents.

It may be recalled here that the experiments with hydrated ferric oxide* were not in accordance with the observations of Mecklenburg, and the exponential constants for the different samples of ferric oxide varied to a considerable extent. In view of those results, the difference in the amounts of adsorption of arsenious acid by hydrated chromium oxide has been shown in the accompanying graph Fig. 1 and the logarithmic curves Fig. 2 have also been plotted. It will be observed that though there was no real equilibrium, the curves all approximate to straight lines, and hence the behaviour is exactly the same as that in the case with ferric hydroxide. In Table XV the values of the constant N for the two different samples of chromium hydroxide are shown.

* Compare Part I of this series of papers

TABLE XV

	N	1/N		N	1/N
No. 1	4.8	0.208	No. 2	5.5	0.182

It will be observed therefore that in this case also, the value of N differs with different samples.

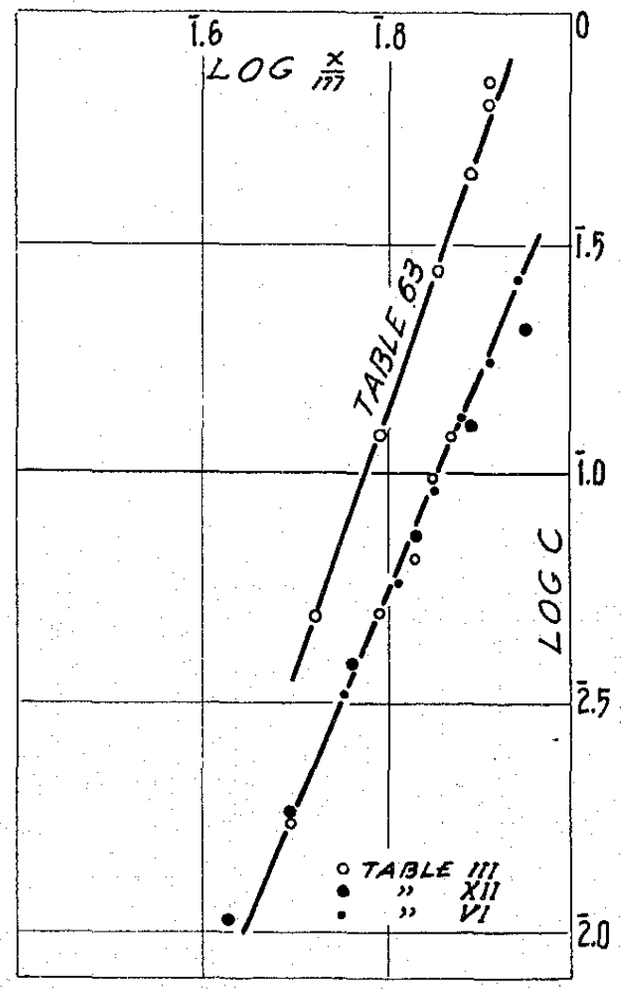


FIG. 2

Having thus studied the adsorptive power of chromium hydroxide for arsenious acid and sodium arsenite under various change of conditions, the adsorption of some mineral and organic acids from solution has been investigated. The sample of hydroxide used in the following experiments is the same one obtained from chromic chloride and ammonia. The time has been 20 hours and other conditions remain the same. The amount of Cr_2O_3 used in all the experiments was 0.2610 grams, Table XVI.

TABLE XVI

A = original concentration in milli-equivalents. B = concentration of solution after adsorption. C = adsorption per gram adsorbent.

A	B	C	A	B	C
Adsorption of Citric Acid					
2.3826	0.6626	6.589	1.7200	0.2180	5.755
2.2040	0.5230	6.439	1.4730	0.1070	5.231
1.9840	0.3670	6.197	1.1320	0.0220	4.254
Adsorption of Malic Acid					
2.3826	0.6956	6.465	1.5030	0.1530	5.174
2.0860	0.4780	6.163	1.1320	0.0330	4.212
1.7950	0.2940	5.751			
Adsorption of Racemic Acid					
2.3826	0.7286	6.340	1.4490	0.1200	5.093
2.0690	0.4990	6.013	1.1320	0.0330	4.212
1.7580	0.2820	5.656			
Adsorption of Sulphuric Acid					
2.3826	0.3366	7.838	1.4500	0.0400	5.405
2.0840	0.1840	7.280	1.1320	0.0170	4.273
1.7670	0.0860	6.439			
Adsorption of Oxalic Acid					
2.3826	0.2396	8.213	1.4380	0.0220	5.428
2.0840	0.1210	7.525	1.1320	0.0110	4.295
1.7900	0.0599	6.630			
Adsorption of Succinic Acid					
2.3826	0.8266	5.964	1.4430	0.1960	4.780
2.0690	0.5860	5.680	1.1320	0.0730	4.056
1.7560	0.3690	5.314			
Adsorption of Benzoic Acid					
2.3826	0.9786	5.380	1.4570	0.2930	4.461
2.1050	0.7600	5.152	1.1320	0.1090	3.920
1.7810	0.5210	4.827			
Adsorption of Hippuric Acid					
1.7500	0.4240	5.082	1.2650	0.1310	4.348
1.6030	0.3370	4.849	1.1820	0.0780	4.087
1.4340	0.2180	4.661			

TABLE XVII

Comparative adsorption of some acids when the initial concentration is the same.

Conc. of acid = 2.3826 milli-equivalents per 100 cc

Wt. of Cr_2O_3 used = 0.2610 gr.

Acid	Adsorption per gram adsorbent	Acid	Adsorption per gram adsorbent
Citric	6.589	Oxalic	8.213
Malic	6.465	Succinic	5.964
Racemic	6.340	Benzoic	5.380
Sulphuric	7.838	Hippuric	5.660*

* extrapolated

Having thus studied the adsorption of acids by hydrated chromium oxide, the amounts of adsorption of salts and alkali by this substance were also investigated. The results obtained with sodium arsenite have already been given. No quantitative results with other salts have however been obtained owing to the smallness in the amount of adsorption. In Table XVIII the results obtained with caustic soda are shown. The amount of chromium oxide is the same as used in the experiment with acids.

TABLE XXV

Adsorption of Caustic Soda

Original conc. millie-quivalents	Conc. of solution after adsorption	Adsorption per gram adsorbent
2.3826	1.9435	1.682
1.7670	1.3540	1.582
1.4500	1.0522	1.524

These results show that alkali is also appreciably adsorbed by chromium hydroxide.

Chemical Laboratory,
Allahabad University.
February 8, 1926.

THE COLOR OF SILVER CHROMATE

BY FLORENCE BUSH

Hunt, in 1845, published a paper[1] concerning the effect of light on solutions, stating that metal chromates precipitated from bichromate solution exposed to light, differed many shades in color from that of a precipitate obtained in a solution made and kept in the dark. As an example he mentioned silver chromate, describing the precipitate from the actinized solution as having a "*much more beautiful color*". Unfortunately the investigator did not state his procedure and conditions.

An effort was made to repeat the results. A potassium bichromate solution was made up, one portion exposed to sunlight for several weeks, another kept unexposed. Equal volumes of the solutions were treated with the same volume of silver nitrate solution. In each case the silver chromate precipitated was brick-red and curdy, of identical appearance. Here, at least, the exposure of pure bichromate solution to sunlight had no effect on a precipitate subsequently formed in the solution.

In an attempt to find what conditions would produce a difference in the appearance of the precipitate, the effect of the following factors was examined:

1) Presence of chromium ions
2) " " free acid (small amounts)
3) Temperature increase
4) Rate of mixing solutions

Experimental

1) 1 cc. dilute chromium sulphate solution was added to 10 cc. of both actinized and unexposed potassium bichromate solution and silver chromate was precipitated with silver nitrate solution. A brick-red, curdy deposit came down, similar to that first obtained. Varying the amount of chromium salt added, produced no change in the type of precipitate obtained.

2) A portion of bichromate solution was acidified with N HNO_3 and silver nitrate added. The silver chromate formed in lustrous, plate-like crystals, many shades darker than from neutral solution.

3) A solution containing the curdy precipitate was warmed. On cooling, the presence of the dark, lustrous crystals was observed.

4) Bichromate solution was added to silver nitrate solution at different rates. The slower the addition, the darker colored and more noticeably lustrous were the crystals formed.

Conclusions

From the observations made, it may be stated that it is the rate of precipitation, and not the action of sunlight, which causes a difference in the appearance of the precipitate.

[1] Mem. Chem. Soc., 2, 316 (1845).

Silver chromate has a low solubility in water, and under ordinary condition of precipitation in fairly concentrated solutions, extensive supersaturation is rapidly attained. The precipitate comes down in very finely divided form. Under conditions where supersaturation is reached more slowly, precipitation is not so rapid, the crystals tend to grow relatively more slowly and larger.

Silver chromate has a higher solubility in acid and in hot aqueous solutions than in aqueous solutions at room temperature. In such solutions supersaturation is not so readily attained, the crystals are larger and fewer in number. When the curdy precipitate was heated, the silver chromate dissolved to some extent. Instead of forming the amorphous deposit again, the chromate precipitated in such a way as to increase the size of the crystals already formed.

When the potassium bichromate solution is added very slowly to the silver nitrate the tendency is toward a low degree of supersaturation in respect to silver chromate. A smaller number of crystal nuclei form initially and slow addition of the bichromate causes an increase in the size of the crystals already formed, rather than an increase in the number of crystals present.

These results correspond, at least qualitatively, with the theory of the dispersion of a solid phase worked out by von Weimarn[1] originally. He stated that for crystalline precipitates of low solubility the degree of dispersion of the solid phase depended on the solubility of the substance, the amount of solid which must be deposited to reduce the concentration of the precipitating substance to its solubility value, and on the viscosity of the solution. He formulated his law thus:

$$d = \frac{N_p}{S_p} n$$

Where d = dispersion coefficient; N_p = amount of deposited solid; S_p = solubility of the solid; n = viscosity of liquid. The ratio N_p/S_p he terms the degree of supersaturation. In general, small degree of supersaturation favor the formation of large crystals, and precipitation from solutions having high degrees of supersaturation favors the formation of very finely crystalline or amorphous precipitates.

As a possible explanation for the color differences noted by the original observer in the silver chromate precipitated from actinized and unexposed solutions of bichromate, it might be that he had varied his addition rates for the two solutions without appreciating the effect this would have on the physical condition of the precipitate formed. Any heating due to the light would also have an effect.

Summary

1) Precipitates of silver chromate from actinized potassium bichromate solutions have the same appearance as silver chromate precipitated from solutions unexposed to sunlight.

2) The rate at which the precipitating solution is added to the bichromate solution causes a difference in the color and physical characteristics of the silver chromate formed.

Cornell University

[1] Washburn: "Physical Chemistry", p. 367.

SOME REMARKS ON THE COLLOIDAL THEORY OF CEMENTS

BY TUTOMU MAEDA

There are two rival theories, the crystal and the colloid theories, for the setting and hardening of cements. My studies on the setting and hardening of magnesium oxychloride cement lead me to the conclusion that these two theories are complementary and not antagonistic. The so-called colloid theory must be modified, however, because it uses a colloid explanation for a phenomenon which plays a minor part in the setting and hardening of cements and omits the explanation of more important phenomena from the colloid standpoint.

My studies, so far, have covered the following five topics, and I will discuss the phenomena in view of what I have found. The full details can be found in the original papers.

1. The composition of magnesium oxychloride cement.[1]

2. Viscosity changes during the reaction between magnesium oxide and an aqueous solution of magnesium chloride; and a new consideration with respect to the setting of cements.[2]

3. A study of magnesium oxychloride cement by X-rays.[3]

4. The aqueous vapor pressure of magnesium oxychloride cement, and the state of water in it.[4]

5. The hardening of magnesium oxychloride cement, and the functions of free water, water of crystallization, and adsorbed water.[4]

With the exception of W. Michaelis[5], the supporters of the colloid theory consider that the colloid phenomenon consists in the adsorption of fluid on the surfaces of the solids in the cement mixture. Thus Cavazzi[6] assumes the direct formation of the so-called gelatinous calcium sulphate; but such adsorption phenomena are not limited merely to cement mixtures. They may also occur as the first step in the reaction when any salt is brought in contact with a liquid or a solution. According to my understanding Cavazzi's gelatinous calcium sulphate can be considered as $CaSO_4(0.5+x)H_2O$, which decomposes, as the second step, into $CaSO_4 . 2H_2O$ and $(x-1.5)H_2O$. In this form the colloid theory does not differ much from the crystal theory, for the latter also attributes the setting of cements to the formation of small, interlocking crystals. I wish to ask, however, the function of the water set free $(x-1.5)$ H_2O per mol $CaSO_4 . 2H_2O$. The most important weapon for the supporters of the so-called colloid theory is the function of the added chemicals which modify the rate of setting. Which of the two reactions—the formation of the gelatinous sulphate or the formation of the crystalline sulphate—is

[1] Maeda and Yamane: Sci. Papers Inst. Phys. Chem. Research, **4**, 85 (1926).
[2] Maeda: Sci. Papers Inst. Phys. Chem. Research, **4**, 102 (1926).
[3] Maeda: Sci. Papers Inst. Phys. Chem. Research, **5**, 95 (1926).
[4] In press: All these five papers are written in Esperanto.
[5] Kolloid-Z., **5**, 9 (1909).
[6] Kolloid-Z., **12**, 196 (1913).

influenced by these chemicals? Various chemicals, of course, play an important part in the coagulation of a colloidal system. To which of the two reactions does the coagulation correspond?

The colloid theory does not explain the cause of hardness from a colloid stand-point, but adopts the latter part of the crystal theory. Are there any crystals in a hardened gelatine?

I am willing to accept the hypothesis of the first adsorption of a fluid on the surfaces of the solids in a cement mixture; but I do not consider it important for the phenomenon of setting, because it is evident that an immediate solution of the solids takes place to some extent, since the fluid has some solvent action on the solids. Some $CaSO_4 . 0.5H_2O$ will therefore dissolve in water and some magnesium oxide will dissolve in the magnesium chloride solution. There will certainly be formed, as postulated by the crystal theory, a solution supersaturated with respect to a new solid phase, and this solid phase will be formed sooner or later. Jolibois and Chassevent[1] have already proved by the conductivity method, that this occurs for $CaSO_4 . 0.5H_2O$ and I have showed it for magnesium oxychloride cement by measurements of the viscosity changes according to the method of Wo. Ostwald and P. Wolski[2], though there was more liquid present in both cases than in real cements. Would it, therefore, be just to assume that supersaturation does not occur in the case of real cement mixtures, as some supporters of the so-called colloidal view say? Quite unjust. Owing to the large extent of active surface in the case of real cements, we may suppose that the supersaturation and consequently the recrystallization of a new solid phase occur very quickly, in which case the above-mentioned gelatinous calcium sulphate is not in the form of $CaSO_4 . 0.5H_2O + xH_2O$; but is in the form of $CaSO_4 . 2H_2O + yH_2O$ or $CaSO_4 . 2H_2O + yH_2O + zCaSO_4 . 0.5H_2O$. So far the classical crystalline theory does not offer any serious difficulties; but, if carried further, it fails to explain phenomena and a new colloidal standpoint comes into play. It must be remembered that the so-called colloidal theory cannot here explain anything more because it denies the supersaturation and the recrystallization. When a new solid phase appears from the supersaturated solution, surface hydration, somewhat according to my own term, occurs on the surfaces of very tiny crystal particles, which may have colloidal dimensions. By surface hydration is meant a phenomenon, whose true nature is obscure as yet; but which occurs quite frequently during crystallization. Adsorbed water molecules on the surface possibly explain it, but in the case of magnesium oxychloride cement, $Mg^{\cdot\cdot}$ or Cl' also can take part in the adsorption. But as the ions themselves are hydrated, water molecules here again play parts. In the above example, I have mentioned the surface hydration on $CaSO_4 . 2H_2O$ with the form of $CaSO_4 . 2H_2O + yH_2O$. This recrystallization accompanied by the surface hydration means the beginning of the setting of a cement, because the free water becomes less by changing into the forms of water of crystallization and adsorbed water, of which the latter plays an important

[1] Compt. rend., **177**, 113 (1923).
[2] Kolloid-Z., **27**, 78 (1920).

rôle in the viscosity relation. Here the crystals formed are not effective for the setting by themselves, but through water. According to my view, the adsorbed water acts like gelatine; in the setting of gelatine, it is clear, that no crystals play a rôle. My X-ray diffraction patterns obtained by the powder method, however, show clearly the existence of crystalline $_3MgO \cdot MgCl_2 \cdot {}_{12}H_2O$ in a hardened magnesium oxychloride cement; $_3MgO \cdot MgCl_2 \cdot {}_{12}H_2O$ is a new solid phase formed in the recrystallization; the composition being determined from my phase rule research. But crystals with colloidal dimension may give a diffraction pattern, and therefore the above fact does not prove the correctness of the classical crystalline theory. The surface hydration is very important for the strength of cements, as the adsorbed water film prevents brittleness. The adsorbed water reminds us of a thin water film between two glass plates.

Furthermore, my opinion is against the crystal growth or the perfection of imperfect crystals as the cause of the hardening. Von Weimarn's crystallization theory of colloids[1] is very full of hints for the setting and hardening: it treats the crystallization from a solution, the solubility and the amount of the crystals formed, the viscosity of the medium, and so on. According to his theory, the general scanty solubility of the newly formed solid phase, the large amount of the above phase and the high viscosity of the medium all postulate, that the formed crystals in cement mixtures are very tiny, although they may form large aggregates, and they can remain in the original tiny form for a very long time. But X-ray diffraction patterns taken at intervals will give a decisive answer to the above questions as to the perfection of crystals, for the patterns by and by will become clear, if the perfection of crystals occurs. From my own X-ray research, it became clear, that when the cement mixture contains a comparatively large amount of the liquid part, it gives a clearer diffraction pattern than that of a mixture with less liquid part. The so-called colloidal theory can not obtain any support from von Weimarn's theory, because it denies the crystallization from a solution.

Also from my own researches, it is clear, that added chemicals and the change of the surface property of a solid part influence the velocity of the setting. According to my considerations, the setting means the appearance of a new solid phase, and therefore added chemicals and the change of the surface property of a solid part mean the change of the velocity of the formation of a new solid phase; and the velocity of the formation of a new solid phase is influenced by two factors: the rate of solution of the solid part into the liquid part and the velocity of the recrystallization of the new solid phase. In the case of magnesium oxychloride cement, the casual standing of magnesium oxide in the open air means the decrease of the velocity of the setting and also of the hardness; this means magnesium oxide became less reactive to the solution. Whether added chemicals affect the reactivity of the surface of the solid part or the velocity of the recrystallization of the new solid phase, I do not know clearly. Furthermore I suppose that the degree of the surface

[1] "Zur Lehre von den Zuständen der Materie" (1914).

hydration may also be influenced. Conductivity measurements will give some valuable informations with respect to the effects of added substances and the change of the surface.

According to my researches, the hardening, which means the hardness increase without external change after the setting, is a continuation of the setting, and the loss of water to the external system is not important; the change of free water into the forms of water of crystallization and adsorbed water, however, is very important for the hardening.

Finally I will discuss the function of free water, water of crystallization and adsorbed water. The first added liquid part in a cement mixture means the free water, which is necessary for practical working. The free water then becomes water of crystallization and adsorbed water by the recrystallization process; this change is necessary to increase the hardness, for the existence of the free water means a soft mass. To prevent brittleness, the adsorbed water is necessary, and interlocking crystals without adsorbed water make a brittle mass, as magnesium oxide and water illustrate. From the above considerations, the setting and hardening of cements are not essentially different from the setting of gelatine or starch paste; with cements, however, a gelatinous mass is obtained through the crystallization of tiny crystal particles from a solution with the surface hydration on their surfaces. This means the necessity of both crystalline and colloidal ideas expressed in a new light.

Summary

1. I have studied magnesium oxychloride cement with special reference to its setting and hardening, in order to clear up the mechanism of the above phenomena.

2. From the above studies, I came to the conclusion, that neither the classical crystalline theory, nor the so-called colloidal theory does not account for the true mechanism.

3. I have proposed a theory, which involves both crystalline and colloidal ideas: the crystalline idea is necessary for the recrystallization from a solution; the colloidal idea, for the surface hydration on the new solid phase.

The Institute of Physical and Chemical Research,
Hongoku, Tokyo,
Japan,
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PROPERTIES OF SUBSTANCES AND MIXTURES IN THE CONDENSED STATE AT THE ABSOLUTE ZERO OF TEMPERATURE

BY R. D. KLEEMAN

In a previous paper the writer showed[1] that the internal energy and entropy of a substance or mixture may each be divided into two parts, one of which is externally controllable while the other is not. It was also shown that the controllable entropy and internal energy are each zero when the substance or mixture is in the condensed state under the pressure of its vapor at the absolute zero of temperature. This zero was called for convenience the absolute zero of control. It was also shown that the relations

$$\left(\frac{\partial u}{\partial v}\right)_T = 0 \tag{1}$$

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v = 0 \tag{2}$$

$$\left(\frac{\partial S}{\partial T}\right)_T = 0 \tag{3}$$

$$\left(\frac{\partial S}{\partial T}\right)_v = 0 \tag{4}$$

hold under these conditions, where u denotes the controllable internal energy, S the controllable entropy, c_v the specific heat at the constant volume v, and T the absolute temperature. A number of additional relations will be deduced in this paper from the results already established and well known thermodynamical formulae by means of the Differential Calculus and the postulate that $\frac{\partial^{n+m} p}{\partial_v^n . \partial T^m}$ (where p denotes the pressure) cannot be infinite, which follows from our notions of matter. The importance and use of these relations consists in that they must be satisfied by the general relations holding between various quantities on writing $T = 0$ and $v = v_0$, where v_0 denotes the volume of the substance or mixture in the condensed state at the absolute zero of temperature.

1) From thermodynamics we have

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p \tag{5}$$

where u may be taken to refer to the controllable internal energy, since the uncontrollable part, which is not a function of v and T, would disappear through differentiation. On differentiating this equation with respect to T and n times with respect to v it becomes

[1] J. Phys. Chem., **31**, 747 (1927).

$$\frac{\partial^{n+1}u}{\partial v^n.\partial T} = \left(\frac{\partial^n c_v}{\partial v^n}\right)_T = T\frac{\partial^{n+2}p}{\partial v^n.\partial T^2} \tag{6}$$

The factor of T in this equation is not infinite according to the postulate given, and hence for a substance or mixture in the condensed state at the absolute zero of temperature, or at the absolute zero of control of the substance or mixture, we have

$$\frac{\partial^{n+1}u}{\partial v^n.\partial T} = \left(\frac{\partial^n c_v}{\partial v^n}\right)_T = 0 \tag{7}$$

since $T = 0$. The specific heat will possess this property if it can be expressed by the equation

$$c_v = \phi_1(v, T) \,.\, \phi_2(T) \tag{8}$$

where $\phi_2(T) = 0$ when $T = 0$. It possesses then also the property expressed by equation (2). It should be noted however that c_v may have the property expressed by equation (7) without having the form given by equation (8).

Every specific heat equation obtained from quantum and other considerations should obey equation (7). A test of the correctness of the assumptions underlying the equation is thereby afforded.

2) Equation (4) may be written

$$\left(\frac{\partial S}{\partial T}\right)_v = \frac{1}{T}\left(\frac{\partial u}{\partial T}\right)_v = \frac{0}{0}$$

at the absolute zero of control, according to equation (2) and since $T = 0$. By means of the Differential Calculus the limiting form on the right hand side of the equation may be written

$$\left(\frac{\partial S}{\partial T}\right)_v = \left(\frac{\partial^2 u}{\partial T^2}\right)_v$$

and therefore according to equation (4)

$$\left(\frac{\partial^2 u}{\partial T^2}\right)_v = \left(\frac{\partial c_v}{\partial T}\right)_v = 0 \tag{9}$$

We have seen in the paper quoted that equation (2), which is Nernst's specific heat theorem, follows directly from thermodynamics. Equation (9) expresses another property of the specific heat which also depends directly on thermodynamics. Experimental evidence of its truth already exists. According to Debye's formula for the specific heat of a monatomic solid[1], which is found to agree well with the facts, the specific heat near the absolute zero of temperature is given by

$$c_v = aT^3 \tag{10}$$

where a is a constant. This equation has been specially investigated by Kamerlingh Onnes and found to be in close agreement with experiment[2].

[1] Ann. Physik, (4) **39**, 789 (1912).
[2] Comm. Phys. Lab. Leiden, No. 147 (1915).

It evidently agrees with equation (9). It is highly desirable that experiments be also carried out with mixtures near the absolute zero of temperature, to determine if their specific heats also satisfy equations (2) and (9), as they should if the deductions on which the equations rest are sound.

3) Equation (4) may be written

$$\left(\frac{\partial S}{\partial T}\right)_v = \frac{1}{T}\left(\frac{\partial u}{\partial T}\right)_v$$

which on being differentiated with respect to T at constant volume becomes

$$\left(\frac{\partial^2 S}{\partial T^2}\right)_v = \frac{1}{T}\left(\frac{\partial^2 u}{\partial T^2}\right)_v - \frac{1}{T^2}\left(\frac{\partial u}{\partial T}\right)_v = \frac{0}{0} - \frac{0}{0}$$

the right handside assuming a limiting form on account of equations (2) and (9), and since $T = 0$. On obtaining the value of the limiting form by means of the Differential Calculus the equation becomes

$$\left(\frac{\partial^2 S}{\partial T^2}\right)_v = \frac{1}{2}\left(\frac{\partial^3 u}{\partial T^3}\right)_v \qquad (11)$$

It expresses a relation between S and u at the absolute zero of control.

4) On differentiating equation (5) with respect to v it becomes

$$\left(\frac{\partial^2 u}{\partial v^2}\right)_T = T\frac{\partial^2 p}{\partial v.\partial T} - \left(\frac{\partial p}{\partial v}\right)_T$$

Since $T = 0$ and its factor is not infinite according to the postulate given, the equation should be written

$$\left(\frac{\partial^2 u}{\partial v^2}\right)_T = -\left(\frac{\partial p}{\partial v}\right)_T \qquad (12)$$

The right hand side may be evaluated by means of the equation of state, remembering that $T = 0$ and $v = v_o$, where v_o denotes the volume of the substance or mixture in the condensed state at the zero of control. Similarly it can be shown that

$$\left(\frac{\partial^n u}{\partial v^n}\right)_T = -\left(\frac{\partial^{n-1} p}{\partial v^{n-1}}\right)_T \qquad (13)$$

5) In general we have

$$\partial S = \frac{1}{T}(\partial u + p\,.\,\partial v)$$

which may be written

$$\left(\frac{\partial S}{\partial v}\right)_T = \frac{1}{T}\left(\frac{\partial u}{\partial v} + p\right) = \left(\frac{\partial p}{\partial T}\right)_v \qquad (14)$$

by means of equation (5). On differentiating this equation $n-1$ times with respect to v we have

$$\left(\frac{\partial^n S}{\partial v^n}\right)_T = \frac{\partial^n p}{\partial v^{n-1}.\partial T} \qquad (15)$$

The right hand side of this equation may be evaluated by means of the equation of state. It is of interest to compare this equation with equation (13).

6) For an adiabatic change we have directly that

$$\left(\frac{\partial u}{\partial v}\right)_S = -p \tag{16}$$

On eliminating p from this equation by means of equation (5) we obtain

$$\left(\frac{\partial u}{\partial v}\right)_S = \left(\frac{\partial u}{\partial v}\right)_T - T\left(\frac{\partial p}{\partial T}\right)_v \tag{17}$$

For any state of the substance at the absolute zero of temperature we therefore have

$$\left(\frac{\partial u}{\partial v}\right)_S = \left(\frac{\partial u}{\partial v}\right)_T \tag{18}$$

This equation expresses that an adiabatic change at the absolute zero of temperature is not attended by a change in temperature. Hence the adiabatic corresponding to zero entropy in a diagram expressing the relation between v and T lies entirely on the v axis, or at least infinitely close to it. This result follows also from the fact that the entropy corresponding to any point in the space enclosed by the positive v and T axes is larger than that corresponding to the point v_o on the v axis.

7) From the previous Section it follows directly that

$$\left(\frac{\partial v}{\partial T}\right)_S = -\infty \tag{19}$$

$$\left(\frac{\partial p}{\partial T}\right)_S = \infty \tag{20}$$

$$\left(\frac{\partial u}{\partial T}\right)_S = \infty \tag{21}$$

for a substance or mixture in the condensed state at the absolute zero of temperature, which includes the absolute zero of control. It may be noticed that equation (19) also follows from the fact that when ∂v is taken positive the temperature, since it is zero, cannot decrease any further, or $\partial T = -0$.

From thermodynamics we have

$$\left(\frac{\partial S}{\partial v}\right)_p = \left(\frac{\partial p}{\partial T}\right)_S \tag{22}$$

and

$$\left(\frac{\partial v}{\partial T}\right)_S = -\left(\frac{\partial S}{\partial p}\right)_v \tag{23}$$

and hence at the absolute zero of control we also have

$$\left(\frac{\partial S}{\partial v}\right)_p = \infty \tag{24}$$

$$\left(\frac{\partial S}{\partial p}\right)_v = -\infty \tag{25}$$

8) From equations (14) and (3) we have

$$\left(\frac{\partial p}{\partial T}\right)_v = 0 \tag{26}$$

at the absolute zero of control.

9) In general

$$\left(\frac{\partial u}{\partial T}\right)_v + \left(\frac{\partial u}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_S + p \left(\frac{\partial v}{\partial T}\right)_S = \left(\frac{\partial S}{\partial T}\right)_S = 0$$

for an adiabatic transformation, which may be written

$$\left(\frac{\partial u}{\partial T}\right)_v + T \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_S = 0 \tag{27}$$

by means of equation (5). At the absolute zero of control we may write the equation in the form

$$\infty = \left(\frac{\partial v}{\partial T}\right)_S = -\frac{\left(\frac{\partial u}{\partial T}\right)_v}{T\left(\frac{\partial p}{\partial T}\right)_v} = -\frac{0}{0}$$

according to equations (19), (26), and (2). This equation may be written

$$\infty = \left(\frac{\partial v}{\partial T}\right)_S = -\frac{\left(\frac{\partial^2 u}{\partial T^2}\right)_v}{T\left(\frac{\partial^2 p}{\partial T^2}\right)_v + \left(\frac{\partial p}{\partial T}\right)_v} = -\frac{0}{0}$$

by means of the Differential Calculus, the right hand side again assuming a limiting form on account of equations (26) and (9), and the equation $T = 0$. This equation may therefore be written

$$\infty = \left(\frac{\partial v}{\partial T}\right)_S = -\frac{\left(\frac{\partial^3 u}{\partial T^3}\right)_v}{2\left(\frac{\partial^2 p}{\partial T^2}\right)_v + T\left(\frac{\partial^3 p}{\partial T^3}\right)_v}$$

by means of the Differential Calculus. Now in order that the right hand side of this equation may be ∞ we must have

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0 \tag{28}$$

whatever the value of $\left(\frac{\partial^3 u}{\partial T^3}\right)_v$ may be.

This equation and equation (26) are of considerable importance. Every equation of state has to satisfy them, and they are therefore of use to de-

termine the proper form of the equation of state. Evidently van der Waals' equation does not satisfy these equations, and this equation of state has therefore not the fundamentally correct form. It is an important problem to find an equation of state which will satisfy these equations of condition.

As an example of the value of these equations in helping to determine the form of the equation of state let us write it in the form of the series

$$p = \frac{ART}{v} + \frac{a_1 + a_2T + a_3T^2}{v^2} + \frac{b_1 + b_2T + b_3T^2}{v^3} \qquad (29)$$

where A, a_1, a_2, a_3, b_1, b_2, b_3 are constants. Equations (28), (26) and the equation $p = o$ give

$$o = a_1 + \frac{b_1}{v_o}$$

$$o = RA + \frac{a_2}{v_o} + \frac{b_2}{v_o^2}$$

$$o = a_3 + \frac{b_3}{v_o}$$

taking into account that $T = o$ and $v = v_o$, the conditions under which the quoted equations hold. The foregoing equations express relations between the constants of the equation of state and v_o.

10) On differentiating equation (5) twice with respect to T at constant volume it becomes

$$\frac{\partial^3 u}{\partial v.\partial T^2} = \left(\frac{\partial^2 p}{\partial T^2}\right)_v + T\left(\frac{\partial^3 p}{\partial T^3}\right)_v$$

On taking into account equation (28), that $\frac{\partial^3 p}{\partial T^3}$ is not infinite according to the postulate given, and that $T = o$, the equation becomes

$$\frac{\partial^3 u}{\partial v.\partial T^2} = \frac{\partial^2 c_v}{\partial T.\partial v} = o \qquad (30)$$

If the specific heat is expressed by the general equation (8) it will satisfy the foregoing equation if either

$$\left(\frac{\partial \phi_1}{\partial v}\right)_T = o \qquad (31)$$

or

$$\left(\frac{\partial \phi_2}{\partial T}\right)_v = o \qquad (32)$$

Along the same lines it can be shown that

$$\frac{\partial^{2+n} u}{\partial v.\partial T^{2+n}} = \frac{\partial^{2+n} c_v}{\partial v.\partial T^{1+n}} = (1+n)\left(\frac{\partial^{2+n} p}{\partial T^{2+n}}\right)_v \qquad (33)$$

where n can only have positive and zero values, and the right hand side can be evaluated by means of the equation of state.

11) On differentiating equation (14) with respect to T and taking account of equation (28) we obtain

$$\frac{\partial^2 S}{\partial v . \partial T} = 0 \tag{34}$$

an equation parallel in form to equation (7) when $n = 0$.

Again on differentiating the same equation $n + 1$ times with respect to T we obtain

$$\frac{\partial^{n+2} S}{\partial v . \partial T^{n+1}} = \left(\frac{\partial^{n+2} p}{\partial T^{n+2}}\right)_v \tag{35}$$

where the right hand side may be evaluated by means of the equation of state.

12) The equation

$$\left(\frac{\partial p}{\partial T}\right)_v = 0$$

given in Section 8 expresses that $\partial p = 0$ on increasing the temperature of the substance at constant volume. Since the pressure is initially zero it follows that it remains zero, and in keeping the volume constant we therefore exercise no constraint. This result will therefore also hold if the volume is unrestricted, or

$$\frac{dp}{dT} = 0 \tag{36}$$

the differential coefficient which is total applying to a substance under the pressure of its own vapor.

Along the same lines it can be deduced from equation (28) that

$$\frac{d^2 p}{dT^2} = 0 \tag{37}$$

Thus the equation quoted may be written

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_v = \left(\frac{\partial x}{\partial T}\right)_v = 0$$

It expresses that $\partial x = 0$ on increasing the temperature of the substance at constant volume. Since x is initially zero (equation 26) it remains zero, and we are therefore exercising no constraint in keeping the volume constant. Therefore the constraint may be supposed removed, giving

$$\frac{dx}{dT} = 0$$

and since we have already seen that the volume constraint may be removed from $\left(\frac{\partial p}{\partial T}\right)_v$ or x we finally obtain equation (37).

The foregoing equations are of considerable importance. The vapor pressure equation of a substance or mixture, which connects the vapor pressure with the temperature, must satisfy them. They evidently express that near the absolute zero of temperature the vapor pressure p is given by

$$p = a_1 T^{2+a_2} \tag{38}$$

where a_1 and a_2 are positive quantities depending only on the nature of the substance. This equation could be tested experimentally by means of a special device for measuring low gaseous pressures, such as the one depending on ionisation. Its experimental proof would be direct evidence of the fundamental results established in the previous paper on the basis of thermodynamics.

13) In the previous Section we have seen that keeping the volume of a substance constant on increasing the temperature by ∂T does not act as a constraint. The unrestricted volume therefore does not change on change of temperature, and we may therefore write

$$\left(\frac{\partial v}{\partial T}\right)_p = 0 \tag{39}$$

and

$$\frac{dv}{dT} = 0 \tag{40}$$

since p is zero and remains zero on change of temperature.

It was also shown that keeping the volume constant during the change ∂T^2 did not act as a constraint. The volume therefore did not change, and we may therefore write

$$\left(\frac{\partial^2 v}{\partial T^2}\right)_p = 0 \tag{41}$$

$$\frac{d^2 v}{dT^2} = 0 \tag{42}$$

The equation of state of a substance must obey equations (39) and (41), and the equation connecting its volume with the temperature when in contact with its vapor must obey equations (40) and (42). The volume temperature equation will evidently assume the form

$$v = v_0 + b_1 T^{2+b_2} \tag{43}$$

near the absolute zero of temperature, where b_1 and b_2 are positive constants depending only on the nature of the substance or mixture, and v_0 denotes its volume in the condensed state at the absolute zero of temperature. This equation may be tested experimentally by measuring the expansion with change in temperature of the solidified substance near the absolute zero of temperature. It may be noted that if p and v can be expanded in powers T by Taylor's Theorem, as is very likely, a_2 and b_2 in equations (38) and (43) are each equal to unity.

14) For the entropy of a substance in contact with its vapor we may write

$$\frac{dS}{dT} = \left(\frac{\partial S}{\partial v}\right)_T \frac{dv}{dT} + \left(\frac{\partial S}{\partial T}\right)_v$$

The differential coefficients on the right hand side are zero according to equations (3), (4), and (40), and hence we have

$$\frac{dS}{dT} = 0 \tag{44}$$

If the condition is imposed that the pressure is to remain constant the former equation becomes

$$\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial S}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p + \left(\frac{\partial S}{\partial T}\right)_v$$

The right hand side is zero according to equations (3), (4), and (39), and hence we have

$$\left(\frac{\partial S}{\partial T}\right)_p = 0 \tag{45}$$

On differentiating the first equation of this Section totally with respect to T it becomes

$$\frac{d^2S}{dT^2} = \frac{d}{dT}\left(\frac{\partial S}{\partial v}\right)_T \frac{dv}{dT} + \left(\frac{\partial S}{\partial v}\right)_T \frac{d^2v}{dT^2} + \frac{\partial^2 S}{\partial v . \partial T}\frac{dv}{dT} + \left(\frac{\partial^2 S}{\partial T^2}\right)_v$$

According to equations (40), (42), and (11) this equation may be written

$$\frac{d^2S}{dT^2} = \left(\frac{\partial^2 S}{\partial T^2}\right)_v = \frac{1}{2}\left(\frac{\partial^3 u}{\partial T^3}\right)_v \tag{46}$$

Similarly it can be shown that

$$\left(\frac{\partial^2 S}{\partial T^2}\right)_p = \frac{1}{2}\left(\frac{\partial^3 u}{\partial T^3}\right)_v \tag{47}$$

15) The change in internal energy of a substance in contact with its vapor is given by

$$\frac{du}{dT} = \left(\frac{\partial u}{\partial v}\right)_T \frac{dv}{dT} + \left(\frac{\partial u}{\partial T}\right)_v \tag{48}$$

The right hand side is zero according to equations (1), (2), and (40), and hence we have

$$\frac{du}{dT} = 0 \tag{49}$$

If the condition is imposed that the pressure is to remain constant equation (48) becomes

$$\left(\frac{\partial u}{\partial T}\right)_p = \left(\frac{\partial u}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p + \left(\frac{\partial u}{\partial T}\right)_v \tag{50}$$

The right hand side is zero according to equations (1), (2), and (39) and hence we have

$$\left(\frac{\partial u}{\partial T}\right)_p = 0 \tag{51}$$

The specific heat c_p at constant pressure is given by

$$c_p = \left(\frac{\partial u}{\partial T}\right)_p + p \left(\frac{\partial v}{\partial T}\right)_p \tag{52}$$

which becomes

$$c_p = 0 \tag{53}$$

by means of equations (51), (39) and since $p = 0$.

The specific heat c of a substance under its vapor pressure is given by

$$c = \frac{du}{dT} + p. \frac{dv}{dT} \tag{54}$$

which becomes

$$c = 0 \tag{55}$$

by means of equations (49), (40), and since $p = 0$.

16) *On differentiating* equation (48) totally with respect to T it becomes

$$\frac{d^2u}{dT^2} = \frac{d}{dT}\left(\frac{\partial u}{\partial v}\right)_T . \frac{dv}{dT} + \left(\frac{\partial u}{\partial v}\right)_T \frac{d^2v}{dT^2} + \frac{\partial^2 u}{\partial v . \partial T} \frac{dv}{dT} + \left(\frac{\partial^2 u}{\partial T^2}\right)_v$$

The right hand side is zero according to equations (40), (42), and (9), and hence

$$\frac{d^2u}{dT^2} = 0 \tag{56}$$

On differentiating equation (50) with respect to T keeping the pressure constant we obtain

$$\left(\frac{\partial^2 u}{\partial T^2}\right)_p = 0 \tag{57}$$

according to equations (39), (41), and (9).

Equation (54) on differentiating it totally with respect to T becomes

$$\frac{dc}{dT} = 0 \tag{58}$$

taking into account equations (57), (36), and (42).

Equation (52) on differentiating it with respect to T at constant pressure becomes

$$\left(\frac{\partial c_p}{\partial T}\right)_p = 0 \tag{59}$$

taking into account equations (57), (26), and (41).

It may be pointed out that the results obtained in the foregoing Sections, omitting those in Sections 1, 4, and 5, cannot be deduced from Nernst's theorem or the third law of thermodynamics, but the general result obtained by the writer is necessary of which they form a part, namely that the controllable internal energy and entropy of a substance or mixture is zero in the condensed state under the pressure of its vapor at the absolute zero of temperature, and that this zero fulfils the mathematical definition of a minimum according to the Differential Calculus. The results in Sections 1, 4, and 5, are deduced directly from well known thermodynamical formulae.

The subject may be further developed along similar lines, which will be carried out in a subsequent paper.

NEW BOOKS

Catalysis in Theory and Practice. *By Eric K. Rideal and Hugh S. Taylor. Second edition. 22 × 16 cm. pp. xv + 516. London and New York: Macmillan and Co., 1926. Price: $6.00.* The first edition was a good book (**24**, 76), and the second is a better one. The chapters are entitled: early history; criteria of catalysis; homogeneous reactions; the theory of heterogeneous catalytic reactions; promoters—mixed, supported, and protected catalysts; catalyst poisons and the inhibition of homogeneous chemical reactions; processes of oxidation; hydrogen and hydrogenation; dehydrogenation; catalysis in nitrogen fixation; hydration, hydrolysis, and alcoholysis; dehydration; colloidal catalysts; catalysts in organic chemistry; catalysis in electrochemistry; catalysis by radiant energy; catalysis in analytical chemistry.

The specific action of catalysts appears clearly in the case of the water-gas reaction, $CO + H_2O \leftrightarrows CO_2 + H_2$, with two catalytic agents, copper and oxide of iron, p. 12. "Over the range 200°-300°C. copper is more efficient than iron oxide as a catalyst for this reaction. Above 300° C., however, iron oxide is quite definitely the more efficient, and, in the region of 400°-450° C., equilibrium conversions are readily achieved. With copper, at these temperatures, a relatively low and decreasing efficiency is found. Armstrong and Hilditch show that this varying efficiency and order of efficiency may be attributed to the differing mechanisms whereby the reaction in question is achieved. Whereas, in the case of copper, the products appear to be formed via formic acid as an intermediate stage, in the presence of iron oxide an alternate reduction of the oxide by carbon monoxide and oxidation of the reduction product by steam apparently occur. It is evident from this, also, that mechanism cannot be involved in the criteria of catalysis."

"This change in physical state of the catalyst is generally attributed to its activity in a series of cyclic actions in which the material participates, the final reaction of the cycle resulting, however, in the regeneration of the catalytic material in its initial form. Thus, in the well-known action of manganese dioxide in promoting the decomposition of potassium chlorate with evolution of oxygen, it has been observed that, if initially a crystalline form of the oxide be employed, the final product is manganese dioxide in the form of a fine powder. The researches of Sodeau have associated this change in physical state with the participation by the manganese oxide in the process of chlorate decomposition. Langmuir compares the changes that occur in the surfaces of metals used as catalysts with the "offsetting" of tantalum filaments, or improperly made tungsten filaments, when run in lamps on alternating current. The offsetting consists of a slipping of the crystals of the metals along the boundary planes, and, in extreme cases, it leads to a disintegration of the structure of the metal. The effect has been shown to be dependent upon the rapidity of temperature fluctuation. The same is true of the surface of the target in an X-ray tube run on alternating current. Introduction of gases intensifies the effect. Langmuir concludes that, in all these cases, the disintegration is to be ascribed to sudden fluctuations in temperature between adjacent atoms in the metal," p.14.

"The more closely a reaction system approximates to that of an ideal system, whether gaseous or in solution, the more nearly independent of either the catalyst employed or the concentration of catalyst does the equilibrium become. As the condition of ideality is approached, the more closely proportional are activity and concentration, "p.18.

"The problem of the solvent in the reaction process may also be examined from the standpoint of the solvation of the reacting species. If a reactant, A, undergoing change, forms, in a solvent, S, a solvated molecule, the equilibrium condition being represented by the equation A + nS = A.nS, the solvent may exercise a profound influence on the rate of change....

"Bjerrum has discussed some of these factors in a recent paper. He points out that the enhanced activity of hydrogen ions in presence of neutral salts, first noted by Arrhenius, can be explained on the basis of varying hydration of the ion. If the ion in the intermediate complex formed by collision of the reacting species and the hydrogen ion have a smaller water content than the ion in the solution, the Arrhenius effect must result. Bjerrum points out

that, if the difference in the two amounts to n moles of water, then the catalytic activity will increase, with decreasing vapour pressure of the solution p, to an extent proportional to $(p_o/p)^n$, where p_o is the vapour pressure of pure water.

"Bjerrum further points out that, besides these catalytic effects which may be associated with the formation of definite chemical compounds, and in which the catalyst, so to say, opens up a number of parallel reaction paths, there are certainly cases where the presence of materials foreign to the actual reaction process may actually exert an influence on the reaction speed without actually entering into combination with the reactants. These act by virtue of the molecular forces which they exert on the reacting complex, changing its form without the production of a chemical compound. A deformation of the reaction complex may occur which may have marked influence on the velocity of rearrangement of the complex. There is some evidence that such deformation catalysts are present in some catalytic gas reactions. Bjerrum points out that the relationship between deformation and activity will be slight. The acitvity of a substance at the same concentration is known to be greater in poor solvents than in good solvents. But it cannot thereby be concluded that the substance will react more rapidly in the poor solvent. Rather should one conclude that the reaction will proceed more rapidly in the good solvent, because, in this case, the greater solubility is an index of greater molecular forces which may influence the velocity of change by deformation," p.21.

"In 1906 Trautz, and independently both McC.Lewis and Perrin, suggested that the energy of excitation be obtained from radiation normally existing and flowing through the reaction system. Perrin was led to this point of view by consideration of the mechanism of unimolecular actions. For such actions the probability of a particular isolated molecule decomposing within the next second is invariant, since the velocity constant is independent of the concentration. The critical energy increment can evidently only be supplied by some non-material type of energy transfer such as radiation, either in the infra red or other portion of the spectrum. Trautz and Lewis were led to the same view by a supposed analogy between photochemical and thermochemical reactions. The extraordinary simplification which would be introduced into chemistry if chemical activation were always produced by the absorption of radiation is the great attraction of the radiation hypothesis," p.28.

"We have noted that the simple radiation theory of chemical action is certainly not tenable, and that many drastic amplifications are required before this attractive conception can be made reconcilable with experimental data. The somewhat arbitrary hypotheses necessary for this purpose have led many to reject *in toto* the conception of activation by radiation and to inquire how far it is possible to assume activation by collision. According to this view, when molecules impinging on one another with such initial speeds that the available energy in the case of a simple bimolecular reaction between molecules of mass m exceeds the critical energy increment, or $(1/4).m\,V^2 > E_c$, they do not suffer elastic collision but undergo activation and disruption. The data of Hinshelwood and Pritchard, on the bimolecular decomposition of chlorine monoxide, of nitrous oxide, and of Bodenstein on hydrogen iodide, strongly support this view," p.35.

"The considerations advanced in the preceding sections may be applied to the more complicated cases of liquids. We have noted that unimolecular reactions in gaseous systems are extremely rare and must conclude that the same is true in solution; thus, cases of dynamic isomerism, *e.g.* acetoacetic ester, cannot be satisfactorily explained on the hypothesis of an intramolecular reaction, although this view is still maintained by some investigators. In solutions, also, complexes or solvates may be formed; the study of bimolecular reactions in gases indicates a possibility that the reaction of tautomeric change may take place through activation by collision between solvents and solute molecule, but, as we shall note, the critical energy increment is high and the reaction velocity negligible at ordinary temperatures. It is for this reason that it is probable that most reactions in solution occur through the intermediary of ternary complexes, reactant, solvent, catalyst. In order to justify this point of view, we must determine the evidence in favour both of the existence of such complexes

and also why such complexes are more easily activated and thus undergo reaction more readily than the simpler binary constituents also present in the system," p.46.

In the case of the inversion of sugar, "the investigations of Lapworth and Dawson, as well as the numerous experiments on neutral salt action, have made it more than probable that it is the unhydrated or the less hydrated form of hydrogen ion which is the active agent," p.50.

"Whilst on surfaces of most liquids the Gibbs layer is but unimolecular in thickness, it cannot be said that the adsorbed solute possesses all the properties of the pure solute in bulk. Thus, saturation of the Gibbs layer in the case of ethyl alcohol-water mixtures occurs at a concentration of 0.3 molar, yet the surface phase, although consisting of pure ethyl alcohol, is by no means identical in properties with a free surface of ethyl alcohol. Even more definite in this direction are the experiments of Iredale on the adsorption of vapours on the surface of mercury. Whilst the surface tension of mercury is lowered very markedly by the adsorption of a unimolecular layer of vapour such as ethyl acetate, benzene, or water, and the lowering is more pronounced the more closely packed the unimolecular film on the surface, yet the vapour pressure of even a closely packed unimolecular film is less than that over the pure liquefied vapour at the same temperature," p.61.

"The question whether a gas can, when it is maintained above the critical temperature, build up a second or more layers on augmentation of the pressure, is as yet uncertain. Indirect experimental evidence for the multimolecular nature of films of vapours adsorbed on solids is provided by the heats of adsorption. But, as we shall have occasion to note subsequently, the surface of the catalyst is by no means uniform in nature, part possessing strong adsorbing powers with other portions of varying activity; a variation in the amounts of different gases adsorbed at what are apparently saturation pressures may indicate, not films of varying thickness, but a covering of varying fractions of the total exposed surface.

"We may conclude that at solid as well as at liquid surfaces primary adsorption is accompanied by a marked decrease in free energy. The building up of secondary or multimolecular films is, however, a by no means uncommon phenomenon, especially in the case of vapours on strong or powerful adsorbing agents; whilst the forces operating in the formation of the primary unimolecular film are strong, those in the secondary film are weaker. The primary forces may be compared to the valency forces operative in co-ordination compounds, whilst those in the secondary film are more akin to the cohesional forces operative in vapours and liquids," p.72.

"It is probable that, on active metals, the "availability" of the surface varies from gas to gas. On the closely packed facets the adsorption forces, are as we have seen, much weaker than on the more open surfaces, and gases which are not readily adsorbed, such as the non-polar, more perfect gases, will not be adsorbed strongly on the crystal facets. On the other hand, polar and easily liquefiable gases will be adsorbed over the entire surface.

"This differentiation in the strength of union between adsorbate and adsorbent is also exemplified in the adsorption of oxygen at charcoal and some metal surfaces. It is found, for example, that if oxygen be adsorbed on to a charcoal surface three types of surface compounds can be identified. A small fraction of the oxygen may be removed as such by evacuation, a larger portion may be removed as carbon dioxide by exhaustion at relatively low temperatures, whilst a third more stable portion into which the other forms are gradually converted is only removed at very high temperatures in the form of carbon monoxide and carbon dioxide. Whilst three forms of carbon surface, the diamond, the paraffin or chain, and the ethenoid (to which the black colour is due), are undoubtedly present, the alteration in the type or the strength of union between the superficial and the underlying carbon atoms is reflected in the alteration in the carbon oxygen linkage. Rideal noted that oxygen could be adsorbed on a nickel surface in two forms, one readily reducible by hydrogen at low temperatures, and the other similar to a superficial coating of nickel oxide only reducible at realtively high temperatures. These observations have been extended and confirmed by Larson in the case of copper," p.77.

"It has already been observed that in many heterogeneous gas reactions, such as the decomposition of alcohols and esters at the surfaces of metals and metallic oxides, the rate of decomposition is independent of the pressure, an experimental fact readily intelligible on the assumption that the reactants are strongly adsorbed and that the reaction velocity actually measured is the rate of conversion of the adsorbed reactants and subsequent evaporation of the products. At sufficiently low pressures a departure from zero order reaction is to be anticipated. Such zero order reactions are frequent in liquid systems. We find, for example, that many enzyme reactions such as the hydrolysis of sugars as observed by Armstrong, Hudson and Nelson, obey within wide limits such a law," p.86.

"Ipatiew appears to have been among the first to record in detail promoter action in a heterogeneous system. He found that in the presence of copper oxide, and in a copper tube, amylene was only one-third converted into isopentane by hydrogen at 200 atmos. at a temperature of 300° C. in twenty-eight hours; with copper oxide in an *iron* tube complete conversion was effected in twelve hours under the same conditions. The same relation holds also for the hydrogenation of tetrahydrobenzene, tetrahydrotoluene, pinene, and carvene," p.102.

"Whitsell and Frazer conclude that manganese dioxide is the initial cause of oxidation at low temperatures in Hopcalite mixtures. The oxidation process may be catalytic or occur at the expense of the oxide oxygen. The purer the catalyst, that is, the freer from adsorbed potash, the more rapidly was it able to take up oxygen fast enough to make the process catalytic. This points to a mechanism of alternate oxidation and reduction. Too strong ignition of the preparations, even though alkali-free, gave a dense product resembling natural manganese dioxide and entirely inactive. Whitsell and Frazer also incline to the view that the cupric oxide in a mixture may cut down adsorbed alkali or affect the way it is held, so that its poisonous effect is annulled. They note that pure manganese dioxide and mixtures of this with copper oxide lost oxygen to the air at room temperatures, and that the activity because of this is greatly increased by the fineness of division of the particles," p.116.

"The outstanding example of promoter action in homogeneous systems is the well-known neutral salt effect in reactions catalysed by the hydrogen ions of strong acids. The inversion of cane sugar, the hydrolysis of esters, the dehydration of hydroxy acids to form lactones, keto-enol tautomerism, and other reactions catalytically accelerated by the use of strong acids, all provide this interesting case of promoted catalysis. If, in addition to a strong acid, a neutral salt of that acid is added to the reaction mixture, it is found that the velocity of reaction is increased. As the neutral salt alone has no appreciable catalytic effect, the case is one of simple activation or promoter action rather than of co-activation. It is beyond the scope of this section to detail all the work which has been accomplished or the varied views which have been put forward to explain this phenomenon. They will be separately treated in subsequent sections of the book. It is desirable, however, to point out here that the many attempts which have been made to account for the phenomena all have this in common, that they attempt to account for the observed acceleration by assumptions, for which experimental evidence is also sought, as to the concentration of either the catalyst or the reacting species or both. And these belief is common to all the investigators concerned that, when the several factors shall have been successfully stated, the observed acceleration will be found to be consonant with the ordinary laws of reaction kinetics. This attitude of mind might well be adopted by workers in all branches of the study, not only of promoter action but also of catalysis generally," p.116.

"In the case of the hydrogen-chlorine combination it is known that the nitrogen-containing organic inhibitors are consumed on the course of the reaction. Their effect, therefore, decreases progressively as the reaction proceeds, and it is to the presence of such bodies that the well-known phenomenon of the induction period in photo-halogenations is to be ascribed. As regards the function of oxygen in the inhibition of the hydrogen-chlorine combenation, Weigert and more recently Rideal and Norrish have shown that chlorine sensitises the reaction between hydrogen and oxygen to visible light, and that oxygen is removed

from the reaction mixture as water vapour. The reaction velocity is proportional to both the chlorine and the oxygen concentration, so that it seems that the excited chlorine molecule transfers its energy by collision to an oxygen molecule, rendering it reactive thereby. With regard to the traces of oxygen normally present in the mixtures used in the studies of the hydrogen-chlorine combination, no special experiments have been made to ascertain what products results from their presence nor the mechanism of their inhibitory action. Bodenstein assumed that the oxygen was, in some manner, maintained at constant concentration throughout the reaction. This point requires further study in view of the above study with higher concentrations of oxygen. The presence of oxygen, however, even in small concentrations, decreases the length of the chain reactions initiated by the absorbed light, and, as far as present data show, to an extent proportional to its concentration in the hydrogen-chlorine mixture," p.151.

"The catalytic activity of oxides of iron and manganese in the Claus process is usually attributed to the property these elements have of forming more than one oxide, thus permitting the assumption of an oscillating oxide acting as oxygen carrier:

$$\begin{array}{ccccc} Fe_2O_3 & \longleftarrow & O_2 & \longrightarrow & O_3Fe_2 \\ \downarrow & & \uparrow & & \downarrow \\ H_2S & \longrightarrow & Fe_2O_2 & \longleftarrow & H_2S. \end{array}$$

Some experiments by some writers, however, indicate that iron sulphide is an intermediary compound in the process of oxidation, and that the mechanism of oxidation can be more truly represented on the following lines, making the Claus process simply an extension of the ordinary gas-works process of spent oxide revivification:

$$Fe_2O_3 + 3H_2S \leftrightarrows 2FeS + 3\,H_2O + S,$$
$$4FeS + 3O_2 \leftrightarrows 2\,Fe_2O_3 + 4S,$$" p.189.

"The investigations on the direct oxidation by means of oxygen gas of a number of organic substances has indicated that the process cannot take place by means of a simple addition,

e.g. $$2X + O_2 + 2XO,$$

where X is the substance undergoing oxidation to the stable oxide XO. The classic researches of Schönbein indicated clearly that, in many cases of oxidation, for every molecule of oxygen consumed a molecule of oxygen was simultaneously converted into a more active state; this active oxygen could then secondarily react either with more oxygen to form ozone, with water to form hydrogen peroxide, or in the presence of other oxidisable substances could oxidise them, frequently causing oxidations which cannot be accomplished by ordinary atmospheric oxygen," p.213.

"Hydrogen may also be produced from water gas by liquefaction of the carbon monoxide at the temperatures of liquid air boiling under reduced pressures. By this method complete separation of the constituents of the water gas is not readily attainable and, in common practice, a hydrogen containing from 2 to 3 per cent of carbon monoxide is generally obtained. A more complete separation of the two gases may only be obtained with a prohibitive decrease in the yield of hydrogen, since a mixture of hydrogen with 2 per cent of carbon monoxide behaves almost exactly like hydrogen in its physical properties. Actually, the yield of hydrogen would be considerably increased if a 95 per cent hydrogen were obtained by the liquefaction process, the remaining 5 per cent of carbon monoxide being subsequently removed by other means," p. 228.

"Whilst the primary formation of methyl alcohol on the surface of the zinc oxide catalyst apparently proceeds smoothly through the formate, the subsequent production of long chain hydrocarbons and their oxy-derivatives appears to be more complicated. As efficient catalysts, oxides or iron impregnated with strong alkalis at 400°-420° C. and 150 atmospheres may be used. The resulting product contains relatively large quantities of isobutyl

and higher alcohols up to C_9, isobutyric and higher acids up to C_9, isobutyric aldehyde and higher aldehydes, acetone and higher simple and mixed ketones, about two per cent of esters, one per cent of hydrocarbons, and a small quantity of waxy solid.

"The mechanism of formation of these long chains can be interpreted in various ways. Since the combination of a hydrogenating catalyst and a strong alkali are required to effect catalysis, this suggests the following sequence of reactions:

(1) $CH_3OH + CO \longrightarrow CH_3COOH$ on the alkali.

(2) $CH_3COOH + H_2 \longrightarrow CH_3CHO$ on the hydrogenator.

(3) $CH_3CHO + H_2 \longrightarrow C_2H_5OH$ on the iron.

The process commences again with ethyl alcohol as reactant.

"If this mixture be heated to 400°C. in an autoclave the alcohols and aldehydes are decomposed and a mixture of saturated and unsaturated hydrocarbons are obtained, a suggestive method for the formation of natural naphthenic petroleum from water gas," p.259.

"The production of hydrocarbons other than ethane in the hydrogenation of acetylene is to be attributed to the same cause, the setting at liberty of the two CH radicals leading to combinations of various forms. Sabatier and Senderens, by treating acetylene with hydrogen in presence of nickel, obtained as much as 20 c.c. of a clear yellow liquid comparable with natural petroleum, possessed even of a slight phosphorescence as is usual with the natural product, and in which higher saturated hydrocarbons, such as pentane, hexane, heptane, octane, nonane, decane, etc., were all present. By suitable modifications of the *modus operandi*, yields of liquid could be obtained with properties corresponding in different samples with the various petroleums from different oil-bearing districts. The different types of oils were produced with such success that Sabatier suggested the theory that many such natural oils had been formed in such manner by catalytic action of metals on mixtures of gases in the earth's interior. This work forms an important contribution to the subject of the origin of petroleum oils," p 278.

"Two alternative theories have been advanced to interpret the mechanism of the first or disintegrating stage of the cracking process, that of Berthelot and the more recent one of Bone and Coward. According to Berthelot disruption proceeds in stages with the primary elimination of hydrogen, with or without the simultaneous formation of methane and the production of an olefinic hydrocarbon containing one or more double bonds. . . .Bone and Coward, on the other hand, advanced the nascent radical theory. On this view the hydrocarbon is considered to be at least momentarily split up into radicals, $\equiv CH$, $=CH_2$, and $-CH_3$, having a fugitive existence and undergoing immediate polymerisation to more complex hydrocarbons, usually, however, simpler than the original raw material," p.291.

"In the arc process developed by Pauling the arc is struck between horn-shaped iron electrodes. The arc is blown upwards between the horns by a powerful blast of air. At the tips of the horn the arc breaks and starts anew at the base. Rossi on examination of the method found that the yields were lower than those in the Birkeland-Eyde or Schönherr processes, and noted that small particles of iron oxide were ejected from the electrode surfaces by the air blast. The iron oxide was found to accelerate the decomposition of nitric oxide at temperatures below that at which a "frozen" equilibrium is normally obtained. By replacement of the iron electrodes by water-cooled aluminium horns this difficulty was eliminated," p.304.

"Mann and Williams discovered that a mixture of a mineral oil and sulphuric acid promotes the formation of esters, and this factor has proved of importance in the development of a practicable commercial process for the production of alcohols. Clough and Johns have given details of the product of such commercial operation, the products in all cases being secondary alcohols, the range extending from isopropyl to secondary octyl alcohol," p.317.

"The fidelity with which the Brönsted theory, as here indicated, interprets the varied manifestations of neutral salt effect in these several reactions, as contrasted with the complete inability of other theories to interpret so varied a behaviour, merits, for the theory, the closest attention and consideration of the student of homogeneous catalytic action," p.348.

"Considerable attention has been given to the mechanism of ethylene production from vaporised alcohol in contact with dehydration catalysts. Ipatiew concluded that the reaction occurred in two steps. Senderens believes that the formation of ether and ethylene are two independent reactions, but Pease and Yung do not think that his early evidence was decisive. Adkins and Nissen pointed out that, in their studies, a given alumina catalyst causes the formation of the same amount of ethylene from ethyl ether that it does from ethyl alcohol, although there is twice as much water formed from the alcohol as there is from the ether. Pease and Yung showed, as a complicating factor, that ether may decompose to give one molecule of alcohol and one of ethylene. These latter authors conclude that the reaction to yield ethylene occurs in steps and that it is not necessary to assume direct dehydration to ethylene, although this is a possible mechanism. From a study of the rate of dehydration of alcohol and ether on titania, Bishoff and Adkins show that ether is only one-half as reactive at 430° as alcohol is at a temperature of 400°. They conclude from this that ethyl ether is not an intermediate stage in the production of ethylene," p.358.

"Kailan and Neumann have studied the reaction velocity in alcohol and alcohol-water mixtures. They find that the formation of lactone proceeds much faster in 99 per cent alcohol than in water, both in presence and absence of hydrochloric acid as catalyst. They show also that water exerts a much more marked retarding action on the catalytic process than is found in esterification processes. With increasing additions of water to the alcohol the velocity falls below thet in pure water, shows, therefore, a minimum such as is found in the decomposition of diazo esters in alcohol-water mixtures.

"Taylor and Close have also studied the velocity of lactone formation in ether and in ether-water solutions, using hydroxymethyl benzoic acid. They found a negligible reaction velocity in dry ether which was tenth normal with respect to hydrogen chloride. This result seems definitely to establish that undissociated molecules have no catalytic activity. They found, however, that in ether saturated with water and also tenth normal with respect to hydrogen chloride the velocity of formation of the lactone, phthalide, was extremely rapid as compared with the velocity in aqueous hydrogen chloride or in acid solutions containing dissolved ether. This result very definitely establishes the fact that the reaction velocity is not directly proportional to the acid concentration or to the hydrogen-ion concentration, since this latter is very much greater in water solution than in ethereal solutions, if measured by conductance of the solutions.

"The result obtained is, however, in qualitative agreement with the theory that it is the activity function of the catalyst which determines the reaction velocity. For, from distribution experiments, it is known that hydrogen chloride distributes itself between ether and water in such a way that more than 99 per cent of the acid is in the aqueous layer. Comparison should therefore be made of reaction velocities in the two solvents not at equal concentrations but at concentrations in the distribution ratio of the hydrochloric acid in the two solutions," p.361.

"Mailhe and de Godon claim that zirconia is as good an esterification agent as titania. Milligan, Chappell, and Reid have studied the esterification process extensively and conclude that silica gel is a better esterification catalyst than either. They do not find that beryllia is a catalyst, contrary to the views of Hauser and Klotz. The researches of Adkins and his co-workers set the matter of the suitability or otherwise of a catalyst in a somewhat different light. They conclude that it is much more the form of the catalyst material rather than the particular dehydration oxide catalyst which governs the suitability for the dehydration process. They find, for example, that aluminas prepared from different starting materials, such as precipitated alumina, aluminium-mercury couples, aluminium alkoxides, show very variable behaviour in esterification activity. The same also is found

to be true for titania catalysts from different sources or different methods of preparation. They ascribe this varying behaviour to a varying spatial relationship of the active centres of the catalyst surface due to varying distances of such centres—a point of view developed by Langmuir to account for activation of catalyst materials. It would be advantageous if some definite proof of such a spatial arrangement of active centres could be brought forward. As yet the assumption is, in reality, an *ad hoc* hypothesis, accounting for known experimental facts. It may be that only a certain fraction of the oxide surface is in reality catalytically active and that this is not the plane surface but the molecules which are detached from the normal crystal lattice, in a state of unsaturation. This latter point of view is that suggested by data on the poisoning of catalysts, adsorption by catalysts, and the data of promoter action in other types of catalytic process," p.375.

"Whilst the original suggestion of Helmholtz that over-potential was caused by the presence of small bubbles present on the electrode surface has received support from investigators such as Möller and MacInnes and Adler, it has been shown in numerous investigations that whilst the formation of bubbles which affect the current density by covering up part of the electrode electrolyte interface may cause slight fluctuations in the over-potential, the phenomenon itself is due to the pressure of some electromotively active form of hydrogen in the electrode. According to Newbery, Glasstone, and others this electromotively active form of hydrogen is present in the electrode as a chemical compound in the form of a hydride of definite chemical composition. It is, however, questionable whether these hydrides do actually exist, and even if they were present whether their properties would be such as to be electromotively active with a virtual solution pressure greater than for gaseous hydrogen. It is more than probable, as Tafel pointed out, that, on the discharge of hydrions, the hydrogen atoms subsequently react to form hydrogen molecules on the surface. If the metal exerts a marked catalytic activity for the surface recombination of hydrogen atoms, the concentration of atoms on the surface will at all times be low. Thus the over-potential, which is a measure of the concentration of the electromotively hydrogen atoms on the surface, will be small for metals (catalytically active) in promoting the union:

$$2H \rightarrow H_2.$$

This view in several modified forms has been supported by the experiments and considerations of Bancroft, Bennett and Thompson, Rideal and Westrip, and others. Metals with high overvoltages will possess a high surface concentration of bound hydrogen atoms when current is flowing. They will have only a small tendency to dissociate hydrogen molecules and will thus exert but a small catalytic activity for hydrogenation processes in which the activation of the hydrogen is necessary," p. 426.

The authors are a bit non-committal on passivity, p. 436, and they seem to think that the actual mechanism is not clear whereby insolubility takes place when light acts on bichromated gelatine, p. 456. The reviewer does not sympathize with any discussion of the Welsbach mantle, p. 103, which ignores the selective emission by ceria. Since light causes chromic acid to go to chromic oxide in presence of gelatine or alcohol, one feels that Luther and Forbes must have missed something when they find, p. 455, that chromic acid is not the light-sensitive agent in the oxidation of quinine by chromic acid.

Wilder D. Bancroft

Physico-Chemical Methods. *By Joseph Reilly, W. N. Rae, and T. S. Wheeler. 22 × 14 cm; pp. xi + 725. New York: D. Van Nostrand Company, 1926. Price: $8.00.* "Some ten years ago, two of us, neither of whom had, at the time, a wide acquaintance with actual technical practice in chemistry, met for the first time in a large works laboratory. We were struck by the numerous instances in which physico-chemical problems arise in such laboratories, and how in many cases it was difficult to find a good account of the more important methods employed in various branches of physical chemistry, and especially of work on precise physico-chemical measurements. On the one hand there were the books which

were intended for student practice at the undergraduate stage, and these did not pretend to treat the subject from the point of view of the postgraduate or technical chemist. On the other hand there were the original papers of authors contained in the various scientific journals, but these in many cases were not readily accessible and the material was not correlated.

"We agreed that a textbook which approached the subject of practical physical chemistry from the Industrial Chemists' standpoint was very desirable and would have been extremely useful to us, and we resolved that if at some time in the future the opportunity occurred we would attempt to provide or produce such a book. During the last ten years we have had considerable experience in technical and applied chemical work and with an additional colleague (T. S. W.) now offer the present work in the hope that it will be of real value to both technical chemists and postgraduate science students."

The sections are entitled: introduction, with chapters on the scope of physical chemistry, experimental errors, nomography, the slide rule, and triangular diagrams; the physical chemical laboratory and its equipment, with chapters on the lay-out of the laboratory, stirrers, shakers, and centrifuges, ovens and evaporators, thermostats, and pumps; general operations, with chapters on laboratory manipulations, determination of melting-point, distillation, and photography; physical measurements with chapters on length, angular measurement of area, volume, mass, time and its recording, gas and mercury thermometers, the platinum resistance thermometer, thermocouples, radiation and other methods for the measurements of temperature, transition-points, density, coefficient of thermal expansion, measurement of surface tension, viscosity, measurement of pressure, elasticity, compressibility and tensile strength; some properties of solution, with chapters on solubility, the molecular weight of dissolved substances, and distribution or partition coefficients; some properties of gases and vapours, with chapters on vapour pressure and boiling-point, manipulation of gases, the ratio of the specific heats of gases; thermochemistry, with a chapter on calorimetry; optical measurements, with chapters on polarimetry, refractive index measurement, the microscope, spectrometry, colorimetry and nephelometry, photometry, and photoelectric effect; electrical properties, with chapters on determination of the conductivity of electrolytes, electromotive force measurement, transport numbers, preparation of buffer solutions, hydrogen ion determinations, and electrochemistry; miscellaneous, with chapters on rates of reaction, X-ray analysis, and practical methods in colloid chemistry.

"During recent years the solution of equations and evaluation of results have been largely accomplished by graphical methods. The accuracy of graphical construction is on a level with that of the slide rule. Where numbers of calculations from the same formula are necessary, its rapidity is much greater than that obtained by other methods of calculation. Further, such methods afford a general examination of the variation of a result with change in the individual factors.

"Among graphical methods at present in use a foremost place is occupied by nomography, the science of the graphical representation of functions. A general discussion of the subject is given by d'Ocagne in his two works. In the following pages the theoretical development of the subject is not expounded in any detail; the object rather has been to demonstrate the use of the nomogram in certain types of formulae useful to the physical-chemist," p. 20.

On p. 35 the authors differentiate the Gibbs triangular diagram from the Roozeboom triangular diagram, the first being one in which we measure perpendicular to the sides and the second apparently one in which we measure parallel to the sides. Of course, there is only one triangular diagram and a given composition is represented by the same point on either basis. Ostwald seems to have been responsible for the confusion.

The authors do not approve of "the enormous single laboratories such as are sometimes found in universities," p. 38. "It would not be advisable for more than thirty students to work in the same laboratory, and if a larger number has to be catered for at the same period, two or more rooms are generally to be preferred to a single large laboratory." Except at

Cornell, the tendency is away from large laboratories. On p. 39 it is probably a typographical error that inserts a not in the sentence that "in at least some of the more recently constructed physico-chemical laboratories steam is not provided for heating, evaporation, distillation or general laboratory work." The reviewer was interested to learn that laboratory desks are often made black with aniline black, p. 40.

In the discussion of the gas thermometer, p. 225, is the surprising statement that "helium would seem to possess advantages and has been suggested by Callendar; like nitrogen it does not pass through substances." This can only refer to metals because helium passes through porcelain or quartz much more readily than hydrogen does.

On p. 280 is the statement that "with white tin and grey tin in a solution of stannic chloride at 5°C the former goes into solution and the latter is deposited, an E.M.F. of a few millivolts being set up." Nobody could deposit any kind of tin from a stannic chloride solution. The reviewer wonders whether there is any record as yet of any appreciable amount of grey tin having been deposited electrolytically at any temperature from any solution. On the same page there is an implied statement that, with ferric chloride and potassium chloride, there is a sharp change from a yellow solution to a red solution at the transition point. This may be true, but it sounds improbable.

Under the flotation method of determining density, the authors say, p. 313, that "the chief error arises from the adherence of a thin layer of air to the surface of the specimen; as a result of this, if the density of a powder is investigated, when the most suitable liquid density has been obtained, some particles will be found to sink and some to rise." The authors have overlooked the adsorption of the liquid or of one of its components. This is the really serious error. Perhaps they thought that adsorption necessarily meant a gas film. It was new to the reviewer that one can get an accuracy of one in five million with a totally immersed float, p. 330.

The authors are much more clear than most people as to what one measures in an ordinary determination of surface tension. "Where the free surface of the liquid is not in contact with its own vapour alone, the force measured is really the interfacial tension of the liquid with the surrounding matter. Thus the interfacial tension varies at the surface is in contact with a gaseous, liquid, or solid medium. Where the liquid surface is in contact with its own vapour mixed with air the interfacial tension does not differ from the surface tension by more than 0.5%. This is the tension usually measured, the conditions for the measurement of the true surface tension being very difficult to attain. The latter constant is thus seen to be a particular case of the general interfacial phenomena," p. 335.

The authors adopt the view of Richards and Carver "that most of the common liquids which wet glass have zero angle of contact if the glass is perfectly clean and the liquids are pure," p. 336. It is a surprise, however, to find no mention of du Noüy in a discussion of measurements of surface tension.

On p. 401 the evaporating tube shown in Fig. 243 is called the Liebig drying tube, though the reviewer had supposed that it was invented in Ostwald's laboratory by Trevor. On p. 405 the authors refer to osmotic pressure to the volume of the solution in which one gram molecular weight of the solute is dissolved and not to the volume of the solvent. Apparently nobody ever reads van't Hoff's papers any more and even Kendall's conversion has had no effect.

"Berkeley and Hartley have examined the osmotic pressures of concentrated solutions, using membranes of copper ferrocyanide capable of withstanding pressures exceeding 100 atmospheres. Equations of the van der Waals type were found to give a good representation of the results with cane-sugar solutions containing 850-180 grams per litre, but since the values of the critical point derived from such equations are impossible, they can only be regarded as applicable over a limited range of values," p. 407.

The reviewer holds no brief for the van der Waals equation. It is purely empirical; but that does not justify this particular criticism. In so far as the so-called constants a and b

are functions of the temperature, which they are, we cannot calculate the critical data unless we reason in a circle and put in the values which hold for the critical temperature. That is what is usually done.

On p. 429 the authors have apparently ascribed Henry's law to van't Hoff. On p. 431 they point with pride to Dawson's calculations of the distribution of acetic acid between chloroform and water. Since acetic acid increases the miscibility of chloroform and water, and since Dawson starts with the assumption that it does not, the admirable constant which he gets illustrates remarkable ability in juggling figures but nothing more. The results should have been presented as showing that agreement with a formula does not necessarily prove anything in regard to the validity of the premises.

"The best results seem to be obtainable by the use of the Vreeland oscillator. This apparatus is noiseless and gives a sinusoidal wave free from harmonics, as shown in Fig. 381 c. It is easy to regulate and does not readily get out of order. The simpler form is arranged to give frequencies of 1,000 or 500 cycles per second, while the larger form gives a frequency which can be varied between 160 and 4,200 cycles per second, and when set will remain constant to within 0.1% for weeks and is not materially altered by the load varying. The apparatus is arranged to work off a 110-volt D.C. and consists of a mercury-vapour tube provided with one cathode and two anodes. The current passes along a split circuit, each arm of which includes a resistance, an inductance and a gap between the cathode and one of the anodes of the mercury-vapour tube; the mercury arc has two symmetrical paths between the cathode and the two anodes. The circuit which produces the oscillations is shunted across the two anodes and contains two inductance coils and a capacity. A current in these coils deflects the arc to one anode more than the other; this produces a potential difference between the two anodes and a larger current passes in the inductance, charging up the condenser. The latter then discharges in the opposite direction, reversing the current in the inductance and the direction of deflection of the mercury arc, and the condenser becomes charged with the opposite sign. This process continues indefinitely, and the working current is taken off by two secondary coils, which may be arranged in series or parallel, according as a high or low voltage is required. When in use the oscillator should not be too near the measuring apparatus and should be surrounded by an earthed sheet-iron case so as to avoid induction effects," p. 579.

The reviewer defies anybody to find out from the text how one really determines the concentration of hydrogen ion. On p. 614 we read that "the hydrogen gas (at atmospheric pressure) electrode in contact with HCl solution, in which the H-ion (not total acid) concentration is also used as a standard." This would be very satisfactory if we were told, as we are not, what concentration of hydrochloric acid is normal with respect to hydrogen ion. The only other clue is the statement immediately preceding, that the calomel electrode "is used as a reference standard in most cases and its E.M.F. taken arbitrarily as zero." That again is true; but it does not tell us how to determine hydrogen ion concentrations and we are left hopelessly in the dark by the paragraph lower down on the same page.

"The normal hydrogen electrode is now generally taken as the standard for reference purposes and its E.M.F. is taken as zero at all temperatures: since we are unable to prepare a solution of HCl which we know to be exactly normal with reference to hydrogen ion concentration, we are compelled to obtain our normal electrode by comparison with a calomel electrode with which it will show a E.M.F. of 0.2828 volt."

In the discussion of the moving boundary method of determining transport number, the authors say, p. 635: "Steele points out that certain conditions must be fulfilled in order to get satisfactory results: (1) the ions must not react chemically on the solutions to be examined; (2) during the electrolysis the solutions must not give rise to new ions, which will move faster than and overtake the measured ion; (3) the indicator ions must have a specific velocity less than that of the ions to be measured; (4) the indicator solution must have a specific resistance not much greater than that of the solution to be measured, and when possible it is better to place the indicator solution above the measured solution, be-

cause, owing to its greater resistance, more heat will be generated, tending to decrease the density of the solution. The correct voltage to be applied in order to get a good boundary must be determined by experiment. With good conductors a narrowed tube may be used, thus decreasing the current and the heating effect. The method is of course only a comparative one and gives values of U/(U+V) only, but knowing the conductivity of the solution and the diameter of the tubes the actual resistance can be calculated, and this, with the value of the current used, enables the potential gradient to be calculated and so the absolute velocities."

The statement in the last line in the preceding paragraph about calculating absolute velocities is not true. The calculation involves the assumption that the migration velocities do not change with the concentration—an assumption which we know to be false in many cases and which may be false in all cases.

On p. 650 there is apparently a typographical error. When discussing the electrolysis of concentrated sodium acetate solution, the authors say that "the gas evolved at the anode is washed with concentrated potassium hydroxide solution to remove the carbon dioxide, which is also evolved with the ethane at the cathode." The last word in the quotation should of course be anode.

Many people will think that it is unwise to dwell at such length on the errors that have appeared in the first edition; but the reviewer does not agree with that. This book is far and away the best of its kind in existence. It should, and probably will, go into every laboratory. The reviewer has already recommended the book to two laboratories and he congratulates the authors on the very successful piece of work that they have done. The very fact that the book is to become the standard reference book makes it essential that the blemishes which are inevitable in a first edition should be removed. Until this can be done, it seems desirable to warn the reader against these shortcomings.

Wilder D. Bancroft

Pyrosole. *By Richard Lorenz and Wilhelm Eitel. 22 × 15 cm; pp. ix + 290. Leipzig: Akademische Verlagsgesellschaft, 1926. Price: 18 marks; bound 20 marks.* The subject is presented under the headings: introduction; subhalides; pyrosols (metal fogs in fused media); pyronephelites (metal fogs in solid media); metal fogs produced by radiation (including luminophores); the latent photographic image; the dispersoids of the mineral world and of slags.

While there is no evidence for the existence of any silver subchloride, it seems pretty certain, p. 37, that there are reddish-violet crystals having the composition CaCl and instable below 800°. Instable crystalline CaI and CaF have also been obtained. There is some electrical evidence for the existence of BaCl, but the compound has not been isolated, p. 38.

Nernst considers that metals belong in a group by themselves, one characteristic being that they do not dissolve in any non-metallic solvent, p. 44, and another being that they are much more opaque than other substances. Lorenz does not concede the first point and does not discuss the second.

Lorenz, von Hevesy and Wolff developed a very ingenious method for titrating a lead fog in a lead chloride melt by adding lead peroxide and noting the color change, p. 50. There is quite evidently a relation between the vapour pressure of the metal and the amount of fog formed, p. 56. In line with the assumption of peptization of the metal by the melt is the fact that a silver fog in fused silver chloride becomes noticeable only after the silver melts.

Cuprous silicate is apparently instable, breaking down into cupric silicate and metallic copper, p. 110. For this reason the authors do not believe that copper-ruby glass is ever cuprous oxide. Glass will take up metallic silver from silver chloride when the conditions are such that silicon tetrachloride is formed, p. 114.

The authors point out, p. 135, that the particles of colloidal gold, silver, etc, are often so small that the color cannot be due to ordinary interference or diffraction phenomena. "It is also characteristic that the color of a given particle does not change perceptibly when the angle of the impinging light changes. [This statement seems to the reviewer to be incorrect.] The simple assumption of a purely molecular resonance is inadequate to account for all the different colors and for the reversible and irreversible color changes which are characteristic of rock salt. The only possible assumption is that such a particle vibrates in groups which contain a larger number of molecules. This assumption was made rather successfully by Kirchner and Zsigmondy in order to account for the color changes in gold-gelatine preparations. Wood has explained in a similar manner the brilliant colors and color changes observed on thin films of the alkali metals prepared by distillation in a vacuum," p. 135.

"In the very many experiments in which phosphors of the alkaline earth sulphides, oxides, and selenides or of the zinc sulphide group were given long exposures, a permanent change of color was observed only in the zinc sulphide phosphors, which blackened. This was first observed by Hausser who studied the blackening of the zinc sulphide phosphors in the light of the mercury lamp behind glass. He reports that a strong heating brought back the phosphorescence completely. Lenard also noticed the decrease in phosphorescence and the blackening which occur on long exposure to ultra-violet light. The blackening of the zinc sulphide by light proved to be similar to the other known chemical effects of light and to be due to a splitting of the molecule. Lenard ascribed the blackening to the formation of metallic zinc, just as the blackening of silver iodide by metallic silver. Pure zinc sulphide, which does not phosphoresce, is also blackened by light. In contrast with the silver halides, water is essential to the blackening of zinc sulphide by light," p. 197.

The authors are inclined to believe that the color of the ruby is due to colloïdal material; but Stillwell has proved that this is not true. On p. 282 the authors speak of well-crystallized KI_3 without giving any evidence for the existence of this hypothetical substance.

This is a very interesting book, but not well written. The emphasis is laid throughout on the fact that Lorenz did this or Lorenz did that. It produces a distinctly bad impression.

Wilder D. Bancroft

Investigations on the Theory of the Brownian Movements. *By Albert Einstein. Translated by A. D. Cowper. 19 × 13 cm; pp. viii + 119. New York: E. P. Dutton ahd Company, 1926. Price: $1.75.* This is a translation and republication of five papers published in 1905-1908. It appears on re-reading that Einstein does not prove that a suspended particle will exert an osmotic pressure. He postulates it from the standpoint of the molecular-kinetic theory of heat, p. 3. "According to this theory a dissolved molecule is differentiated from a suspended body *solely* by its dimensions, and it is not apparent why a number of suspended particles should not produce the same osmotic pressure as the same number of molecules."

Unless one admits that there is no difference between a dissolved and a suspended particle, Einstein's conclusions do not follow at all and get their validity only from the confirmation by the distinctly inaccurate measurements. In other words, Einstein has shown that this assumption enables him to account fairly well for the phenomena of the Brownian movements. There is nothing to show whether one can account for them on any other hypothesis. After Loeb's fiasco with the Donnan equilibrium one cannot be too careful about matters of this sort.

Wilder D. Bancroft

3-966

CATALYTIC REACTIONS OF ETHYLENE

BY HERBERT WARREN WALKER

Objects of the Investigations: To study the products obtained when ethylene is passed over various solid catalysts at different temperatures with special reference to the liquid condensation products. To find out how each catalyst is affecting the ethylene and to discover the catalyst which will yield a high percentage of polymerized ethylene in the form of a liquid oil.

Introductory and Historical

The action of ethylene at high temperatures without the use of any specially prepared catalyst, save what catalytic effect the material of the reaction chamber may have contributed, has been studied by several investigators. Marchand[1] who was the first to make a careful study obtained carbon and hydrogen from ethylene at a "white heat." Magnus[2] working at "red heat" obtained methane, hydrogen, carbon, and naphthalene. Berthelot[3] in several investigations obtained acetylene, ethane, styrolene, and naphthalene.

Norton and Noyes[4] passed a current of ethylene through a red-hot tube and examined the products. They succeeded in identifying benzene, naphthalene, anthracene (?), propylene, butylene, divinyl (butadiene), methane, ethane, and carbon. Only a trace of hydrocarbons of the acetylene series was reported.

Day[5] was the first of the workers on this subject to get away from the use of such indefinite terms as "red heat" and "white heat" to denote the temperature at which he worked. His experiments were carried out at 400°. He obtained, if the gas was heated for sufficient time, marsh gas, ethane, hydrogen carbon, and liquid products.

Lewes[6] found the decomposition did not begin below 600° and concluded that ethylene is primarily resolved into equal volumes of acetylene and methane as a result of $3C_2H_4 = 2C_2H_2 + 2CH_4$, and that the acetylene subsequently either polymerizes or is resolved into its elements according to the temperature.

Bone and Coward[7] starting with a known volume of ethylene determined the changes in the partial pressures of the gas. Ethylene, acetylene, ethane, methane, hydrogen, and aromatic hydrocarbons were present at definite

[1] J. prakt. Chem., **26**, 478 (1842).
[2] Pogg. Ann., **90**, 1 (1853).
[3] Compt. rend., **50**, 805 (1860); **62**, 94 (1866); Ann. Chim. Phys., (4) **16**, 144 (1869) etc
[4] J. Am. Chem. Soc., **8**, 362 (1886).
[5] J. Am. Chem. Soc., **8**, 66 (1886).
[6] Proc. Roy. Soc., **55**, 90 (1894).
[7] J. Chem. Soc., **93**, 1216 (1908).

temperatures over certain time intervals. The primary effect of high temperatures (600°-900°) was to cause an elimination of hydrogen with a simultaneous loosening or dissolution of the bonds between the carbon atoms, giving rise to residues such as $:CH_2$ and $\vdots CH$. These residues (a) form $H_2C:CH_2$ and $CH\vdots CH$ or (b) break down into carbon and hydrogen or (c) hydrogenate to methane in an atmosphere rich in hydrogen. These possibilities may be realized simultaneously in proportions dependent on temperature, pressure, and amount of hydrogen present.

Engelder[1] discovered that at temperatures below 500° ethylene was not decomposed appreciably under the conditions of the experiment, without a catalytic agent. Bradley and Parr[2] found that ethylene decomposed into a mixture of ethane and methane in the neighborhood of 500°. Above 500° the ethane content gradually disappeared, with a resultant increase in methane. Hollings and Cobb[3] observed that around 800° ethylene decomposed into methane and acetylene, while at higher temperatures it went into methane and hydrogen.

Concerning the action of catalytic agents on ethylene not so much data are available as for the pyrogenic decomposition. Sabatier and Senderens[4], in connection with their famous hydrogenation experiments, included an investigation of the decomposition of ethylene. With heating alone, ethylene was decomposed slowly in a tube above 325° giving carbon, methane, and free hydrogen. From our experience with the presence of air or oxygen in the ethylene we conclude that when Sabatier observed the apparent decomposition of ethylene at these low temperatures, some air for an actual combustion of the gas was probably present. With nickel, Sabatier and Senderens observed that if a current of the gas is passed over the reduced metal heated above 300° the nickel is seen to swell up into a voluminous black material which finally fills the tube and chokes it up; all the ethylene disappears and a gas is obtained containing ethane, methane, and hydrogen. In contact with nickel the ethylene was decomposed into carbon and hydrogen, but the latter was taken up at once by a portion of the ethylene to form ethane which is more and more broken down to methane at higher temperatures. With cobalt at 360° and even 425° the ethylene underwent slow carbonization without rapid swelling and much more ethylene survived. The cobalt acted less actively than nickel. Iron did not act till above 350° and gave a still slower decomposition. Platinum black and reduced copper did not have any appreciable action on ethylene. Magnesium powder acting at 600° on methane, ethane, ethylene, and acetylene caused a 95 per cent decomposition. Aluminum powder, near the fusion point of the metal, 660°, caused a total decomposition, while platinum decomposed only 80 percent.

Ethylene with anhydrous zinc chloride at 275° and 70 atmospheres pressure, gives a gas containing 36 percent ethylene, 3 percent hydrogen, and 61 per-

[1] J. Phys. Chem., **21**, 676 (1917).
[2] Chem. Met. Eng., **27**, 737 (1922).
[3] J. Gas Lighting, 126, 97.
[4] Sabatier-Reid: "Catalysis in Organic Chemistry" 326 (1922).

cent saturated hydrocarbons and a complex liquid of which 85 percent is pentane and hexane without any methyl-cyclobutane. The remainder consists of numerous hydrocarbons including unsaturated hydrocarbons boiling above 145° and naphthenes which are particularly abundant around 250°.[1]

Berthelot and Gaudechon[2] submitted ethylene to the action of ultra-violet light produced by a mercury arc lamp. An oily liquid polymer formed, boiling a little above 100°. Yield—11 percent. The residual gas was pure ethylene as analyzed by combustion.

Engelder (loc. cit.) incidentally observed that ethylene is not decomposed by alumina but that titania catalyzes the decomposition to a small extent at 490°—i.e. 4 percent for a rate of flow of gas of one liter per hour.

As has been stated, to find out how different catalysts split ethylene at different temperatures is one of the purposes of our study. The field for the most part is unploughed. No one could have foretold that zinc oxide would be the best catalyst to accomplish the synthesis of methyl acohol from carbon monoxide and hydrogen. Fischer and Tropsch[3] had to discover empirically with years of work that weakly alkalized iron and mixtures of iron and oxides of metals like chromium, zinc, beryllium, etc., as catalysts would serve in the synthesis of petroleum and solid paraffins from carbon monoxide and hydrogen. This apparent success of Fischer at synthesizing gasoline interests us because we hope to obtain a synthetic fuel by polymerizing ethylene. At present, however, Fischer cannot be counted on to let the outside world know in just what ratios he mixes his materials and how he prepares them to get the yields he says he does at ordinary atmospheric pressure.

Theoretical

The decomposition of ethylene by heat and catalytic substances may take place in the following ways:

(a) by splitting off two hydrogen atoms yielding hydrogen and acetylene: $C_2H_4 = C_2H_2 + H_2$,

(b) by the dissolution of the bonds between the carbon atoms to form $:CH_2$ groups, or $:CH$ groups, considering the intermediate product acetylene,

(c) by the direct breaking down into carbon and hydrogen: $C_2H_4 = 2C + 2H_2$.

The acetylene formed as a product of the splitting off of two hydrogen atoms as in (a) may in turn, and probably does, decompose into carbon and hydrogen. Thus the carbon and hydrogen become the products of a consecutive reaction. It will be necessary to point out that acetylene is as unstable as, or better, more unstable than ethylene under some given conditions.

The polymerization of ethylene takes place according to the equation: $xC_2H_4 = (C_2H_4)_x$—a reaction in which the bonds between the carbon atoms are opening up to allow linkage of two or more molecules of ethylene, but not

[1] Sabatier-Reid: "Catalysis in Organic Chemistry" 211 (1922).
[2] Compt. rend., **150**, 1169 (1910).
[3] Ber., **59**, 830 (1926).

broken so that the carbon atoms separate to bring about a decomposition of the ethylene. It will be noted there is a marked change in volume during the process of polymerization, especially if the polymerized product be considered a liquid. Pressure on the reactor should have considerable influence on the quantity of ethylene polymer formed and should diminish the decomposition into C_2H_2 and H_2 (see page 993). With the acetylene formation decreased to a negligible amount or entirely prevented, the carbon produced by its decomposition will be correspondingly eliminated. Elimination of carbon deposition is most essential for a continuous polymerization process because it renders the catalyst inert.

Experimental

Materials. The ethylene is commercial ethylene made from ethyl alcohol and is procured in tanks put up by The U. S. Industrial Chemical Co. The catalytic substances are described in detail below.

Apparatus and Procedure. Fig. 1 shows the essential parts and arrangement of the apparatus. The general procedure was to pass a quantity of gas at a measured rate of flow from a graduated 3 liter cylinder through a purifying and drying chain into the heated tube over the catalyst, and to collect the gaseous products in the graduated cylinder B, connected beyond the furnace. The confining liquid in the cylinder was saturated sodium chloride solution which ran from an over-head beaker through a siphon tube to displace the ethylene and to maintain sufficient pressure to force the gas through the apparatus. The flow of gas was regulated by the stop-cock D.

The purifying chain consisted of a Friedrichs wash-bottle containing alkaline pyrogallol prepared as for regular oxygen absorption in gas analysis (see below), and a similar bottle filled with concentrated sodium hydroxide solution for carbon dioxide removal and to act as an indicator of the approximate rate of gas flow. The drying tubes comprised one of anhydrous calcium chloride, beyond the bottle containing the sodium hydroxide solution, and three phosphorus pentoxide tubes.

A Jena or Pyrex glass tube was used in the furnace K in which to heat the catalyst. Where possible the catalytic material was measured out in a porcelain boat and the boat inserted in the tube. In some instances the material was placed directly in the tube before setting the tube in place in the heating unit. All heating was done in a multiple-unit electric resistance furnace.

A side-arm tube L with an inner seal served, with a test tube J attached, to collect the liquid products. Beyond this stood a manometer M for measuring decomposition and polymerization by presssure changes under what might be called static conditions. The gas-receiving bottle B contained as confining liquid saturated sodium chloride solution in which the gases are only slightly soluble. This bottle was provided with a manometer and outlet tube for the confining liquid.

In each run a rapid stream of ethylene, four or five liters per hour from a twelve-liter bottle, was started through the apparatus and at the same time the heating current turned on. The catalyst was heated gradually from room

temperature. By the time the heating unit reached a temperature of 100° all traces of residual air and gases had been swept out and ethylene alone remained in contact with the catalyst. Now the 3-liter cylinder was connected in place of the bottle and a quantity of ethylene at a measured rate of flow passed through the apparatus. A very uniform temperature could be maintained by regulating the rheostat. Temperatures were determined by a

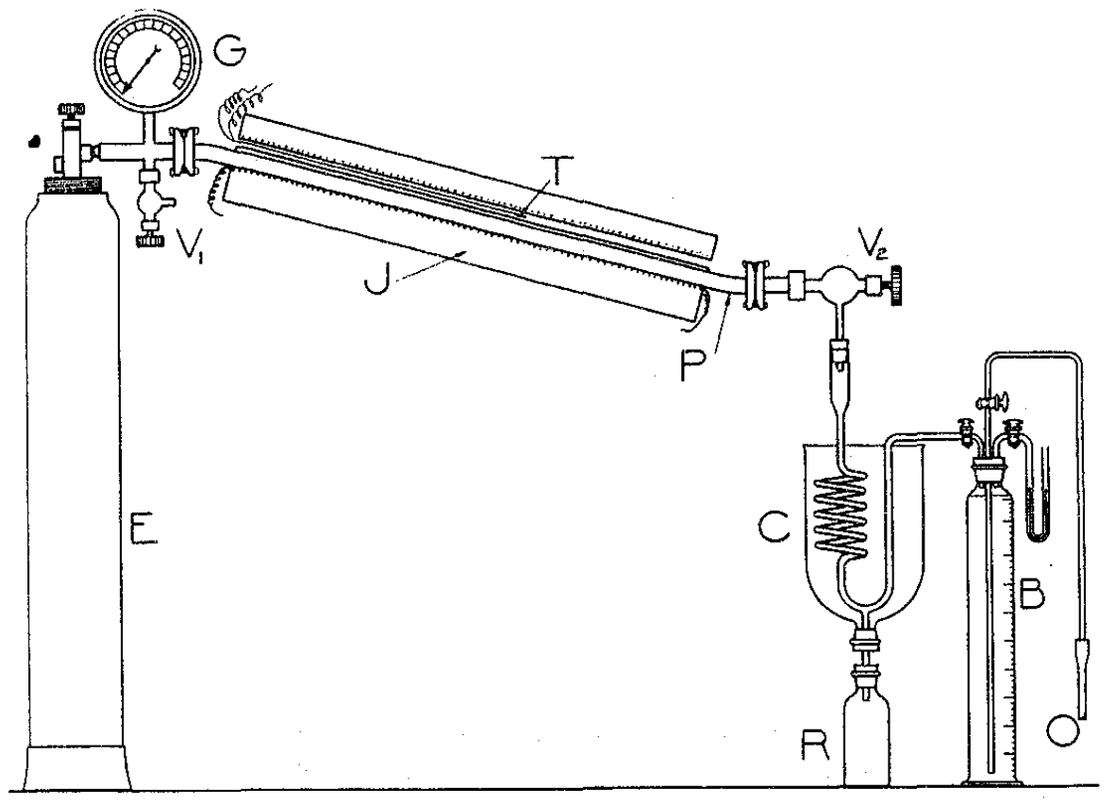


FIG. 1

chromel-alumel thermocouple inserted in the furnace and protected by a Pyrex tube. The millivolt readings on the Leeds and Northrup potentiometer box No. 82184 gave an accuracy of plus or minus five degrees within the values given in Hoskins' catalogue table of millivolts and temperature equivalents for chromel and alumel.

The catalysts, in general, were prepared by calcining the nitrates deposited on pumice and subsequently reducing by hydrogen, if metals. If oxides, they were precipitated as the hydroxides in dilute solution with ammonium or sodium hydroxide. The gelatinous or flocculent precipitates were washed thoroughly by decantation until no test for electrolyte in the filtered supernatant liquid was obtained, filtered and dried in a air oven at 120°. The dry solid was powered in an agate mortar to a 200-mesh fineness.

Analysis of the Gas Mixtures

The methods used in analyzing the gas mixtures are given below. The sample was withdrawn from the receiving bottle and measured in a Hempel burette containing saturated sodium chloride solution as the confining liquid. The various constituents contained in the mixtures were determined as follows in the order given:

1. Carbon Dioxide. This was absorbed in 1 : 1 KOH contained in a Hempel single pipette. The pipette contained rolls of iron wire gauze to give a greater absorption surface.

2. Ethylene and Acetylene. In the earlier part of the work Tucker and Moody's method[1] for determining ethylene in the presence of acetylene, by first passing the mixture into ammoniacal silver chloride solution to remove the acetylene, and then into dilute bromine water for absorption of ethylene, was used. We found that the quantity of ethylene absorbed by the ammoniacal silver chloride varied so with the time the mixture was shaken as to make the method uncertain and impractical. The modified method of Ross and Trumbull[2] for the analysis of mixtures of ethylene and acetylene was tried. Consistent and accurate results were obtained with known mixtures such as could not be obtained by the foregoing method, and so we adopted this means of determining ethylene and acetylene in the presence of one another. In brief, the scheme is to absorb both ethylene and aectylene in fuming sulphuric acid and then to remove the SO_3 fumes by contact in the KOH pipette. The ethylene and acethylene were determined separately as follows:

Ethylene. The percentage of ethylene is taken as the difference between the total percentage absorbed in fuming sulphuric acid and the value obtained for the percentage of acetylene in the sample.

Acetylene. A separate sample of about 50 cc. of the gas is passed into a bulb over silver nitrate solution. After closing a stop-cock in the bulb stem the bulb is disconnected from the burette and shaken until absorption is complete or until there is no further rise of the solution into the bulb. The stop-cock is opened, bulb rinsed, and the acid liberated by the reaction:

$$C_2H_2 + 3AgNO_3 = C_2Ag_2.AgNO_3 + 2HNO_3,$$

titrated in the flask supporting the bulb with standard alkaline solution. Standard alkali is added until the brown color of silver oxide appears. The excess silver in solution is precipitated with 5-10 cc. neutral 20 percent sodium chloride solution. The excess alkali is titrated with standard acid, using methyl orange as indicator. It can be calculated that 1 cc. 0.1 N NaOH solution is equivalent to 1.120 cc. acetylene at standard conditions of 0° C. and 760 mm. pressure. The volume of gas taken as a sample is therefore reduced to the volume it would occupy under standard conditions and compared with the volume of acetylene shown to be present by the alkali required to neutralize the nitric aicd liberated.

3. Oxygen. Alkaline pyrogallol prepared by the method of Anderson[3] i. e. dissolving 15 g. of pyrogallol in 100 cc. of a solution of KOH of specific gravity 1.55, removed all the oxygen with one minute shaking or four passages of gas back and forth.

4. Carbon Monoxide. The reagent for this constituent was ammoniacal cuprous chloride. This was made by adding 25 g. of Cu_2,Cl_2 to 100 cc. of strong

[1] J. Am. Chem. Soc., **23**, 671 (1901).
[2] J. Am. Chem. Soc., **41**, 1180 (1919).
[3] J. Ind. Eng. Chem., **6**, 989 (1914).

NH_4OH to which had previously been added 20 g. of NH_4Cl. After three minutes shaking in a double pipette, the ammonia fumes given off by the reagent were removed by passing the gas into a pipette containing 5 percent H_2SO_4.

5. Hydrogen. This gas was determined by fractional combustion over CuO heated to 250-270°. The contraction in volume gives directly the percentage of hydrogen. Before admitting the gas the air contained in the CuO tube must be displaced with nitrogen and a measured volume of nitrogen must be passed through the tube at the end of the determination to sweep out all the hydrocarbon residue for the subsequent combustion analysis.

6. Methane and Ethane. These gases were burned with a measured volume of oxygen in a Dennis combustion pipette. From the contraction in volume observed after the combustion and the carbon dioxide formed, the percentages of methane and ethane can be calculated. The formulas are:

$$C_2H_6 = (2/3)\ (2CO_2 - \text{T. C.}),$$

$$CH_4 = CO_2 - 2C_2H_6, \text{ where T. C. represents the}$$

total contraction observed after combustion.

Zanetti, Suylam, and Offner[1] have shown that ethylene acted on by heat at 750° yields a maximum quantity of butadiene to the extent of 0.0096 liters of butadiene per liter of ethylene or approximately 1 per cent. While this is very interesting theoretically and it is possible that butadiene may be formed at lower temperatures under the influence of certain catalysts the actual yield seemed too small for us to make the long analysis for butadiene for each run when our catalysts did not seem to approach the reaction necessary for giving butadiene as a product. Of course, we, like everybody else who appreciates the role butadiene may play in the synthesis of rubber, would delight in obtaining a 90-100 percent yield of butadiene instead of polymerized ethylene, these hydrocarbon gases mentioned above, and carbon.

The Action of Heat

Thermal Decomposition of Ethylene

The results of passing ethylene through a clean, empty Jena glass tube at different temperatures and at different rates of gas flow are shown in Table I. A rapid stream of gas was started through the apparatus at room temperature to sweep out any residual air and the heating current turned on. At definite fixed temperatures the heating was kept constant, the rate of gas flow diminished to a slow constant speed, and a measured sample of the gas was run through and collected for volume measurement and analysis. Any condensation of liquid products was observed as well as any deposition of carbon on the walls of the tube where heated.

Below 600° no deposition or polymerization occurred. Each sample of collected gas at temperatures below and including 600° showed no change in composition from the ethylene used initially. That is to say, under the conditions of the experiment, ethylene is stable toward the action of heat unless

[1] J. Am. Chem. Soc., **44**, 2036 (1923).

TABLE I

Ethylene through an empty Jena combustion tube.

No. of run	I	II	III	IV	V
Temp. of tube (deg. C.)	500	550	600	650	650
Duration of run, in min.	50	105	65	65	45
Cc. gas passed through	1480	1200	1180	1100	550
Cc. gas envolved	1500	1220	1200	970	530
Cc. gas per min.	29.6	11.4	18.2	17.0	12.2
Percent C_2H_4 before	98.5	98.5	98.5	97.8	97.8
Percent C_2H_4 after	99.4	98.7	99.0	83.5	67.5
Percent decomposition	00.0	00.0	00.0	14.6	31.0
Condensation of oil	nil	nil	nil	small amt.	drops red amber oil
Carbon deposition	nil	nil	nil	very small amt.	small amt.
Analysis of gas:					
Ethylene	99.4	98.7	99.0	83.5	67.5
Acetylene	——	——	——	3.9	8.2
Hydrogen	——	——	——	3.1	4.4
Methane	——	——	——	4.2	12.0
Ethane	——	——	——	2.9	6.5
Total	99.4	98.7	99.0	97.6	98.6

the temperature exceeds 600°. This confirms what Lewes (loc. cit.) found and is of the order of magnitude of temperature required before ethylene begins to be decomposed as observed by Engelder (loc. cit.) and Bradley and Parr (loc cit.).

Above 600°, about 615°, see Table II, ethylene begins to decompose and to polymerize. As would be expected, the slower the rate of gas flow or longer the contact in the heated chamber, the greater the extent of decompsition and the more incresed the polymerization. There is marked increase in the acetylene yield and a corresponding decrease in the ethylene content of the gaseous products with a 12 cc. per minute rate over that for the 17 cc. per minute rate. With two-thirds the rate of flow, as it happened, there was over twice the decomposition. Bone and Coward (loc. cit.) have studied the thermal decomposition of ethylene at higher temperatures, performing experiments as high as 1180°. Our interest for the time stops where the temperature range in which glass tube exerts an effect begins. We can now tell whether it is the glass tube or the catalytic material in question that is exerting an influence and we have the problem of finding what it is in the glass tube that is bringing about this decomposition and, more particularly, the polymerization.

TABLE II

Ethylene through empty Jena tube.
Rate of gas flow—1.5 liters per hour.
Temperature gradually increased from room temperature.

Temperature in degrees C.	Condensation of oil	Deposition of carbon
400	nil	nil
455	nil	nil
510	nil	nil
580	nil	nil
600	nil	nil
615	Light brown oil	Small amount

Attached manometer, passed gas into tube under slight pressure, and closed off tube.

Temperature in degrees C.	Time	Time interval	Reading of lower Hg col., in cm.	Reading of higher Hg col., in cm.	Diff., press. above atm.
615	5 : 20		16.90	26.90	10.00
615	5 : 32	12 min.	19.15	24.50	5.35
Pressure change during interval					−4.65

In order to account for the gaseous products obtained, it may be said (1) the ethylene must have been split between the carbon and hydrogen atoms, thus yielding hydrogen and acetylene: $\begin{matrix} & H & H & \\ - & - & - & - \\ H & - & C : C & - & H \end{matrix} = C_2H_2 + H_2$. We shall show a little later that acetylene is more unstable toward heat than ethylene and since carbon is deposited on the heated tube wall, the acetylene, in part anyway, is in turn breaking down into carbon and hydrogen: $\begin{matrix} H & H \\ \cdot & \cdot \\ C & C \end{matrix} = 2C + H_2$. This progressive break-down shows an increase in volume of the products over the reactants, but (2) the ethylene, simultaneously with the decomposition into acetylene and hydrogen, is polymerizing. The unsatisfied bonds between the carbon atoms are opening up so that one molecule may unite with another until a large aggregate or polymer is formed which exists in the liquid state under ordinary conditions.

$$x\left(\begin{matrix} & H & \\ H & - & C : C & - & H \end{matrix}\right) = (C_2H_4)_x.$$

When this polymerization reaction is taking place, undoubtedly some of the free hydrogen and $:CH_2$ and $\vdots CH$ groups, whose source is given below, link up with the "nascent" ethylene and help build the liquid polymer. The formation of this liquid polymer from the gaseous ethylene is accompanied by a

large decrease in volume and that the net result is a contraction in volume and not an increase as the formation of hydrogen from ethylene would in itself require.

In addition, (3) the ethylene is resolved into $:CH_2$ groups by a division of the molecule between the carbon atoms: $H-\overset{H}{\underset{|}{C}}:\overset{H}{\underset{|}{C}}-H \longrightarrow 2\ :CH_2$,

or the acetylene formed by (1) is splitting bewteen the carbon atoms to produce $\vdots CH$ groups: $H-C\vdots C-H = 2\ \vdots CH$, because methane is among the products. It is known that methane is one of the products of the pyrogenic decomposition of acetylene. The methane results from the hydrogenation of these $:CH_2$ and $\vdots CH$ groups by the hydrogen previously liberated from the ethylene in the acetylene formation. This hydrogenation, whether it takes place according to: $2\ :CH_2 + 2H_2 = 2CH_4$ or $2\ \vdots CH + 3H_2 = 2CH_4$ or both, produces a decrease in gas volume, which effect is added to that occurring with polymerization to the liquid. It is plain to see that any ethane in the product is a result of the hydrogenation of some of the undecomposed ethylene.

Table II shows what happens if a stream of ethylene at the rate of about 1.5 liters per hour is passed through the Jena tube and at the same time the tube heated gradually from room temperature. That a temperature of 615° is required before the ethylene is decomposed or polymerized confirms the results in Table I. At this temperature a manometer was attached to the heating tube, some ethylene passed into the tube to produce a pressure of 10.0 cm. above that of the atmosphere and the tube closed off at the intake. Over an interval of 12 minutes there was a decrease of 4.65 cm. mercury caused by the polymerization and decomposition of the gas.

Thermal Decomposition of Acetylene

In order to determine the relative stability of ethylene and acetylene toward heat under the conditions of our experiments and to find out at what temperature acetylene is breaking down into carbon, hydrogen, and $\vdots CH$ groups, we subjected acetylene to the heat treatment in the clean, empty Jena tube. In Table III are tabulated the measurements made with acetylene at different temperatures and for different rates of gas flow through the tube.

This study shows acetylene to be stable toward heat at 400° at as low a rate of flow as 13.8 cc. per minute. At 450° with this same rate of flow acetylene polymerized, as indicated by the appearance of a brown fluorescent liquid condensing at the cooler end of the tube in minute drops. If at the same temperature the rate of gas flow were increased approximately twice or to 25 cc. per minute no polymerization occurred. At 450° slight decomposition was taking place but the larger tendency was for the acetylene to polymerize as work at higher temperatures shows better.

TABLE III

Acetylene through an empty Jena glass tube

No. of run	I	II	III	IV	V	VI
Temp. of tube (deg. C.)	400	450	450	500	500	550
Duration of run, in min.	60	70	65	80	45	155
Cc. gas passed through	1200	970	1630	1000	1500	2200
Cc. gas envolved	1180	920	1630	675	1320	1220
Difference	00	50	00	325	180	980
Percent contraction	00	5.2	00	32.5	12.0	44.3
Cc. gas per min.	20	13.8	25	12.5	33	14.2
Percent C_2H_2 before	98.5	98.5	98.5	98.5	98.5	98.5
Percent C_2H_2 after	98.4	94.0	96.3	93.8	93.8	87.6
Percent decomposition	00	4.6	2.2	4.8	4.8	11.1
Condensation of oil	nil	min. amt.	nil	brown liq.	less than IV	red amber liq.
Carbon deposition	nil	v. small amt.	nil	small amt.	small amt.	small amt.
Analysis of gas:						
Acetylene	98.4	94.0	96.3	93.8	93.8	87.6
Ethylene	——	5.2	2.2	3.4	5.3	7.8
Hydrogen	——	——	——	1.3	——	1.9
Methane	——	——	——	0.7	——	trace
Ethane	——	——	——	0.3	——	trace
Total	98.4	99.2	98.5	99.5	99.1	97.3

At 500° and 550° we get more marked polymerization and decomposition and these are decreased with increased rate of flow or with shorter contact of the gas with the walls of the tube—orthodox behavior. What is interesting, however, is the tendency acetylene has at those temperatures to polymerize rather than to decompose. The heat effect, combined with any catalytic effect of the glass tube, in opening up the bonds between carbon atoms to allow formation of larger molecules is greater than in splitting off hydrogen and yielding carbon. It is interesting also to analyze and consistently find ethylene among the gaseous products.

The decomposition of acetylene up to 550° does not take place to a large extent. With a rate of gas flow of 14.2 cc. per minute at 550° 87.6 percent acetylene remained undecomposed. What effects we do get are these. First, there is an elimination of the hydrogen atoms depositing carbon: $\overset{H}{\underset{C}{|}}\!\!-\!\!\overset{H}{\underset{C}{|}} = {}_2C + H_2$. Secondly, to a far smaller extent at this temperature, there is the division between the carbon atoms to give :CH groups, for ethylene is not acted upon at this temperature and methane is among the products. The

hydrogen which is set free does three things. It hydrogenates (1) the acetylene part way to ethylene, (Ross, Culbertson, and Parsons[1] prepared ethylene by the hydrogenation of acetylene), (2) the :CH groups to methane, and (3) some of the acetylene to ethane.

In comparing the behavior of acetylene with that of ethylene we observe that acetylene is much less stable toward heat than ethylene—the former begins to polymerize and decompose at 450° while a temperature of 615° is required to polymerize and decompose ethylene. It is to be noted that acetylene is much more inert toward decomposition 100° above the temperature at which it is first acted upon by heat than ethylene is 30° above the temperature at which thermal decomposition and polymerization begin. This merely shows it is easier to open up the bonds between the carbon atoms of acetylene than to split off and eliminate the hydrogen atoms.

TABLE IV

Acetylene through an empty Jena glass tube.
Tube heated rapidly from room temperature to 545°.
Rapid stream of acetylene flowing through, 3 liters per hour.
Manometer attached, passed acetylene into tube under slight pressure and closed off tube at intake.

Temperature in degrees C.	Time	Time interval	Reading lower Hg col., in cm.	Reading higher Hg col. in cm.	Diff., or press. above atm.
545	5 : 04		17.20	26.60	9.40
545	5 : 11	7 min.	29.90	17.65	−8.35
Pressure change during interval					−17.75

Ran acetylene through tube heated to 545° for 20 hours at rate of one liter per hour, attached manometer, passed in gas under slight pressure and closed off tube at intake.

Temperature in degrees C.	Time	Time interval	Reading lower Hg col., in cm.	Reading higher Hg col., in cm.	Diff., or press. above atm.
545	11 : 39		16.65	27.10	10.45
530	11 : 49	10 min.	18.65	25.05	6.40
Pressure change during interval					−4.05

We tried the experiment of running the acetylene continuously through the tube heated to 540° at a rate of flow of one litre per hour. Carbon deposited on the inside walls of the tube, formed a thin layer of lamp black after about 20 hours. The pressure measurements in Table IV show how markedly the catalytic action of the glass is cut down by this carbon deposition, thus indicating that contact catalysis plays a part in the polymerization and that

[1] J. Ind. Eng. Chem., 13, 715 (1921).

activation of the acetylene is not due to heat alone. There was a reduction of 17.75 cm. of mercury in the pressure over a period of 7 minutes at 545° when the gas was first passd through the tube, but after 20 hours heating and passage, over an interval of 10 minutes we got a diminution of only 4.05 cm. mercury pressure. Part of this final reduction is due to a contraction of the gas with the 15 degree drop in temperature, but even so the value shows that the deposition of carbon is rendering the walls inert. During the 20 hours about 3 cc. of a red brown oil were collected. In addition there was the appearance of a heavy viscous oil and some small quantities of naphthalene were found. No effort to analyze this small yield was made, but some analyses of an oil obtained from a gaseous mixture of equal parts ethylene and acetylene passed through the heated tube throw light on the composition of this oil.

Ethylene and Acetylene in Equal Parts through the Empty Jena Tube

The mixture of gases was run to learn the mutual effect of the gases on the liquid product in the presence of one another.

Temperature—600°.

Rate of flow of gases—1200 cc. per hour, A yellow-amber and a deep-red oily liquid condensed on the walls of the tube just beyond the heating until a 15 cc. portion of the product was collected in something like 8 to 10 hours and fractionally distilled under a reduced pressure of 25 mm. mercury. The distillation was carried out in a Claissen flask with a side-arm filled with glass beads and heated in an oil bath. Reduced pressure was obtained by a large water-suction pump. To prevent frothing and bumping, nitrogen was allowed to escape through a capillary beneath the surface of the liquid being fractionated. The first fraction consisted of a clear light yellow oil less viscous than the initial product. Temperature—39°-40°. At 58° heavy vapors came over which solidified in the condenser, due possibly to polymerized styrene. After a second light yellow distillate a heavy viscous oil of deep-red color was left as residue. From this a third fraction was obtained, light yellow in color, before the residue became very viscous, dark colored, and small in amount.

Analysis of Fraction I by organic combustion.

1) Percent carbon—88.97 Percent hydrogen—9.08
Ratio carbon : hydrogen—9.8 : 1.

2) Percent carbon—85.73 Percent hydrogen—8.51
Ratio carbon : hydrogen—10 : 1.

In 2) some unburned vapors escaped because the copper oxide in the combustion tube was not hot enough to burn the vapors carried over by the dry oxygen.

Ratio of carbon to hydrogen in acetylene—12 : 1
" " " " " " ethylene—6 : 1

If two parts acetylene to one part ethylene are in the polymerized mixture the ratio is calculated to be 10 : 1. This fraction is very likely polymerized ethylene and polymerized acetylene mixed together.

Analysis of Fraction III by organic combustion.

1) Percent carbon—92.08 Percent hydrogen—7.26

Ratio of carbon : hydrogen—12.7 : 1.

In acetylene the ratio of carbon to hydrogen is 12 : 1, hence this fraction might well be polymerized acetylene. The condensation products of acetylene and ethylene heated in a Jena glass tube at 600° may then be said to consist of polymerized acetylene and polymerized ethylene in varying proportions.

What is in the Jena glass which is catalyzing the polymerization of ethylene? Can we prepare some single catalytic material in the laboratory that will accomplish the opening up of the bonds between the carbon atoms of ethylene at a lower temperature than that at which the empty tube acts? The composition of Jena glass[1] is as follows:

SiO_2	— 64.58 Percent.	Na_2O	— 7.38 Percent.
Al_2O_3	— 6.28 "	B_2O_3	— 10.03 "
ZnO	— 11.78 "	Fe_2O_3	— 0.10 "
CaO	— 0.08 "	K_2O	— trace
MgO	— 0.12 "	MnO	— trace.

The following substances as catalytic materials were then tried:

Silica Gel as Catalyst

Preparation: 500 cc. 40 percent water glass or sodium silicate solution were diluted to 1200 cc. and heated to boiling. 175 cc. concentrated HCl were diluted to 300 cc. and added slowly to the hot silicate solution with stirring. The precipitated silica was allowed to settle, the supernatant liquid decanted, and a hot water portion added to wash out the NaCl and excess acid. This extraction was repeated until the filtered liquor gave no turbidity with $AgNO_3$. Filtered and dried over night in an air oven at 100°. The dry silica was then pulverized in an agate mortar to pass a 200-mesh sieve.

TABLE V

Ethylene over silica gel

Time	Potentiometer reading in millivolts	Temperature equivalent in deg. C.	Condensation of oil	Change in silica
9 : 40	12.5	305	nil	nil
: 47	14.3	350	"	"
: 56	16.8	410	"	"
10 : 04	20.7	500	"	"
: 08	22.0	530	"	"
: 12	23.0	560	"	"
: 21	24.6	590	"	slightly grey
: 26	25.5	615	v. small amt.	more grey (carbon)
: 33	26.0	625	v. small (fog)	carbon depositing

[1] Hodkin and Cousen: "Glass Technology".

Approximately 1 g. of the silica was placed in a Jena glass tube in the center of the heating unit, the tube connected with the gas source and a rapid stream of ethylene started through the tube. When all the free air had been swept out and replaced by the ethylene the rate of gas flow was reduced to one liter per hour and the heating current turned on. As the temperature increased gradually from the temperature of the room the observations tabulated above were made. The results are typical of many runs in Jena and Pyrex glass tubing. Using a Pyrex tube as a container for the silica similar results were obtained. They are herewith tabulated.

TABLE VI

Time	Potentiometer reading in millivolts	Temperature equivalent in deg. C.	Condensation of oil	Change in silica
5 : 04	12.8	310	nil	nil
: 06	14.8	360	"	"
: 08	16.5	400	"	"
: 18	18.7	455	"	"
: 24	21.5	520	"	"
: 30	24.0	575	"	grey
: 34	25.0	600	"	"
: 38	26.3	635	v. small amt.	carbon deposited

The Pyrex reaction tube and silica were heated to 600°. Keeping the temperature constant, a sample of gas for volume measurement and analysis was collected.

TABLE VII

Ethylene over silica gel

Temp. of furnace in deg. C	650
Duration of run (minutes)	40
Cc. gas passed through	520
Cc. gas envolved	420
Cc. gas per minute	13.0
Percent C_2H_4 before	98.5
Percent C_2H_4 after	76.8
Percent decomposition	22.0
Analysis of gas:	
Ethylene	76.8
Acetylene	0.0
Hydrogen	7.1
Methane	9.1
Ethane	5.1
Total	98.1

During the above run a brown oil condensed very slowly on the walls of the tube to form only a fraction of a cc. The silica became black throughout its mass with complete dissemination of carbon. No appreciable amount of carbon collected on the walls of the tube where heated, because the tube walls were hotter than the silica.

The silica is ineffective over the temperature range below 600°. It does not activate ethylene perceptibly more than the empty glass tube. The changes the ethylene undergoes are those which have been ascribed to the action of the tube alone. One difference, however, is observed. The silica decomposes entirely the acetylene, which is formed by splitting hydrogen from the ethylene. This is shown by the increased carbon deposit and hydrogen yield, and the absence of acetylene in the gaseous products. It is not the silica in the glass tube that activates the ethylene.

Silica plus 1 Percent Borax as Catalyst

The borax used was C.P. sodium borate which had previously been heated at 200° for several hours. The silica and powdered borax were throughly mixed by grinding together in a mortar before placing in the heating tube. The rate of flow and temperature increase was regulated as with silica alone.

At 580° there began a distinct darkening at the first contact of the gas with the silica-borax mixture due to the deposition of carbon. At 650° a sample of gas was collected for analysis, the results of which are as folows: ethylene—78.8, acetylene—0.0, hydrogen—4.8, methane—9.4, ethane—6.3. Meanwhile at this temperature a very small amount of oil had condensed on the sides of the tube and carbon had collected throughout the entire mass of material. The presence of the borax had no effect on the silica activation—the mixture gave results no different from those obtained with pure silica.

Silica plus 1 Percent Sodium Hydroxide

Before placing the mixture of silica and small quantity of caustic soda in the heating unit the two substances were throughly stirred and ground together in a mortar. The treatment was like that for silica alone. When the slowly rising temperature reached 590° the silica commenced to darken with deposited carbon forming over and through it. At 615° the carbon deposit was increasing and liquid products condensing in small traces,—a behavior like that with pure silica. The fused sodium hydroxide probably united with the silica to form a sodium silicate which does not promote the activation of ethylene by silica.

Silica plus 10 Percent Calcium Hydroxide

Calcium hydroxide prepared as described below under Calcium Hydroxide as a Catalyst was mixed with another portion of pure silica to make a 10 percent mixture by weight of the hydroxide. When run in the heating unit in place of silica, no new or different effect was noted than that received with silica alone. Above 600° the white mass of material began to darken with the formation of carbon over it and a very slight condensation of a colorless oil took place at 650°. A gas analysis of the products collected at 650° showed

the presence of the following constituents in these percentages by volume: ethylene—79.8, acetylene—0.0, hydrogen—8.4, methane—5.3, ethane—5.4. These results are in accord with those obtained at this temperature with pure silica alone.

Calcium Hydroxide as Catalyst

The calcium hydroxide used was prepared by precipitating calcium hydroxide from a dilute solution of Baker's analyzed calcium chloride with sodium hydroxide solution and washing with hot water by successive decantations until the filtered supernatant liquid gave no test for chloride ion. The precipitate was filtered, allowed to drain and dried at 130° in an air oven. The dry hydroxide was ground to pass a 200-mesh sieve and kept in a stoppered bottle. During the course of the run carried on in the usual way no condensation of any oily liquid took place and no carbon became deposited up to 650°. Our conclusion is that calcium hydroxide under our experimental conditions has no effect on ethylene. Between 600° and 650° the hydroxide commenced to dehydrate and moisture alone condensed.

Borax as Catalyst

C. P. sodium borate, $Na_2B_4O_7.1.0H_2O$, heated at 240° several hours was pulverized in an agate mortar and placed in a porcelain boat which was pushed into position in the reaction tube. The tube was heated gradually from room temperature with a slow passage of ethylene over the anhydrous borax. The borax proved to be inactive toward the ethylene. No condensation of any oil took place up to 650°. At 570° the borax sintered and above 600° some carbon became deposited on the solid material.

Calcium Silicate as Catalyst

Preparation; 300 cc. of 40 percent sodium silicate (water glass) solution were diluted to 1200 cc. with distilled water and the resulting solution heated to boiling. To the hot silicate solution a hot solution of 55g. $CaCl_2.6H_2O$ in 300 cc. of distilled water were added. The flocculent calcium silicate precipitate settled and the clear supernatant liquid was decanted. Washings with hot distilled water were carried on until no test for the chloride ion could be obtained with silver nitrate solution. Filtered off the insoluble silicate, drained and dried in an air oven at 130°. Ground the dry material to 200-mesh fineness.

Approximately 1 g. of this calcium silicate was placed in a porcelain boat and inserted in a Jena glass tube to a position in the center of the heating unit. The gradual heating and slow flow of gas was carried out as described above. After heating to 625° no condensed polymers appeared. The white calcium silicate showed no change in appearance until a temperature of 600° was reached when a slight darkening occurred due to the deposition of a very small quantity of carbon. This darkening did not increase until the temperature rose above 650° where the carbon formation increased slightly. The decomposition of the ethylene by the calcium silicate at 650° is negligible. What action we are getting is that of the glass tube. A gas analysis of the

product collected at 650° showed the presence of ethylene—96.0 percent, hydrogen—0.7 percent, and methane and ethane—2.6 percent. It is not a calcium silicate in the original tube which brings about a polymerization or decomposition of the ethylene.

Ferric Oxide as Catalyst

Preparation: 20 g. of C. P. ferric nitrate were disolved in 120 cc. distilled water and 20 g. granulated pumice stirred in. The mixture was evaporated to dryness and then heated to dull redness until no more fumes of NO_2 were evolved, stirring frequently. Finally a strong blast-lamp flame was applied to drive off the last traces of nitric oxide. The red brown oxide of iron (ferric) remained on the pumice when cool.

Heated the tube slowly from room temperature with a steady current of gas pasing over the material. At 280° the ferric oxide was partly reduced to black oxide of iron. At 400° continued reduction and no condensation of liquids took place. At 500° a brown oily liquid appeared in very minute quantities. The pumice that held the red-brown ferric oxide now possessed a black lustrous metallic appearance, due to ferroferric oxide and metallic iron resulting from the reduction of the oxide. The gaseous products were not analyzed.

This study of the action of ferric oxide on ethylene reveals that up to 500° no appreciable quantity of liquid polymers condense and that the iron oxide is reduced more or less completely to metallic iron. What liquid products did condense perhaps were the result of the metallic iron which is formed during the run as a product of the reduction. It will be interesting to study the action of finely divided iron itself on ethylene at lower temperatures.

Zinc Oxide as Catalyst

Preparation: 20 g. of C. P. zinc nitrate were dissolved in 120 cc. distilled water and 20 g. granulated pumice stirred in. The mixture was evaporated to dryness and then heated to dull redness until no more fumes of NO_2 were evolved, stirring frequently. Finally a strong blast-lamp flame was applied to drive off the last traces of nitric oxide. When the material cooled, white oxide of zinc remained on the pumice.

In accordance with our usual practice after placing the zinc oxide in position in the reaction tube and sweeping the tube free from residual gases by a rapid stream of ethylene, the heating current was turned on and a slow gas flow of about one liter per hour maintained. With the gradual increase in temperature through the range from room temperature to 600° no condensation of any oil took place. The ethylene was undergoing no polymerization to liquid products in contact with the zinc oxide. A gas sample collected at 525° analyzed for 98.2 percent ethylene, whereas 98.5 percent ethylene had been used initially. At 600° the gaseous product contained 98.0 percent ethylene, indicative of no decomposition of the ethylene at this temperature. The zinc oxide during the heating process in the presence of ethylene is reduced to a small extent. The white oxide begins to darken at about 525° and when removed after heating to 600° possessed a slaty-grey color. The re-

duction products of the reaction between the ethylene and zinc oxide, taking place to only a very small extent at this temperature, are not sufficient in yield to permit quantitative measurement by the ordinary methods. No carbon was deposited on the pumice. In concluding this brief description of the action of zinc oxide it may be said that under the experimental conditions zinc oxide neither polymerizes nor decomposes ethylene, but interacts with the hydrocarbon and it is at the same time reduced.

This reduction of zinc oxide by ethylene raised the question of whether or not ethylene would accomplish the more or less complete reduction of the oxide at a moderate temperature using massive zinc oxide material. This has been tried and the results are described below.

The Reduction of Massive Zinc Oxide by Ethylene

A mass of powered, stock-room zinc oxide was introduced into the reaction tube, connections made with the gas delivering bottle, the current on, and the tube heated gradually from room temperature while a slow stream of ethylene gas passed over the material.

Above 525° the reduction began, as manifested by a change of the white oxide toward a black color. At 600° the mass of oxide became darker. The temperature was kept constant for four hours. During the heating a very small amount of zinc condensed in the cool part of the tube. Cooled tube, removed material. The black-looking powder was actually a grey-black. Examined under the microscope—the black powder could be distinguished from the zinc oxide originally used, but if any zinc was present it was colloidal and adsorbed by the oxide. No liberation of hydrogen was obtained when this product was allowed to interact with hydrochloric acid, using chlorplatinic acid as a promoter. Some finely divided carbon appeared to be present, although a sample of material heated in a gas flame on a spatula was practically all reoxidized to white zinc oxide below red heat.

Another sample of the same zinc oxide was introduced into a quartz tube and heated to 800°-825° with a constant flow of ethylene over the material. The gas was polymerized to a brown oily liquid and to white flakes of naphthalene which condensed in the tube. The zinc oxide was in part completely reduced to metallic zinc which formed in two conditions: 1) as a mirror on the walls of the tube and 2) as grey zinc in an agglomerated mass. Both these zinc products interacted with dilute hydrochloric acid to liberate hydrogen. Very little zinc dust collected by condensation beyond the heated portion of the tube. The vapor pressure of zinc at 800° is 175 mm. (Mellor). The residue consisted of a grey-black powder. The gaseous products were hydrogen, methane, carbon monoxide, and acetylene. The reaction may be represented thus:

$$2ZnO + 2C_2H_4 = 2CO + C_2H_2 + 3H_2 + 2Zn$$

and in addition:

$$5C_2H_4 = C_{10}H_8 + 6H_2$$

by which ethylene polymerized to naphthalene with a splitting off of hydrogen.

Lead Oxide as Catalyst

Preparation: 331 g. lead nitrate were dissolved in 500 cc. hot distilled water and to this solution were added 135 cc. concentrated NH_4OH which had been diluted to 400 cc. and then heated. Heavy white lead hydroxide precipitated and was washed by decantation until a portion of the filtered supernatant liquid gave no test for nitrate ions. Filtered, drained, and dried in an air oven over night. The dry hydroxide was then ground to 200-mesh fineness.

The white lead hydroxide was placed in a porcelain boat, inserted in the glass tube and gradually heated, passing a slow stream of ethylene over the material. Dehydration of the hydroxide began at about 145°. The temperature was increased to 240° and held constant until the material was completely dehydrated, and the whole mass became yellow lead monoxide. As the heating now continued very definite color changes in the lead oxide occurred. At 390°-400° the yellow oxide turned light-red throughout, the color of litharge. At 435° the red mass became brown, due to the presence of a black reduction product, lead suboxide, Pb_2O. Above 490° grey metallic lead was formed on the surface of the red-brown material and at 600° the oxide was reduced completely to metallic lead, a small amount of which distilled over and collected in the cool part of the tube, but for the most part remained in the porcelain boat as lustrous silvery globules.

The change in the white hydroxide of lead or hydrated lead oxide to yellow lead monoxide and to the red lead monoxide at 400° in the ethylene atmosphere are changes one observes if a sample of the white hydroxide is heated in a nitrogen atmosphere. When the white precipitated compound of hydrated lead monoxide dehydrates, the yellow form of lead monoxide results, PbO (yellow). Now if this yellow form be heated to 400° out of contact with air the red lead monoxide, identical in color with litharge, results as a sintered transformation product. It is a matter of the state of subdivision with resultant optical differences and color change. It has been found by Kohlschütter and Roesti[1] that yellow and red forms of lead monoxide are obtained depending on how rapidly the lead hydroxide is allowed to separate from the solution in which it is precipitated. A rapid separation gave $3PbO.H_2O$ in colloidally dispersed, flocculent or clearly crystalline form; while slower separation gave yellow PbO, always well crystallized. Formation of the red PbO followed that of the hydrate. The hydrate, these observers say, was not observed to give yellow PbO from any degree of dispersion. We seem to be dealing with a white hydrate which first yields the yellow form of monoxide upon dehydration and the red form with further heating. It is stated in the same paper that $PbCO_3$ heated in air at 400° gave a red product not Pb_3O_4 which when heated in N_2 changed into PbO yellow at 650° without change of form.

A later paper by Kohlschütter and Scherrer[2] states that x-ray analysis by the powder method now shows entirely different results for yellow PbO and red PbO; values of "d" are 8.70 and 9.27 respectively; yellow PbO by analy-

[1] Ber., **56B**, 275 (1923).

[2] Helvetica Chim. Acta, **7**, 337 (1924); (Chem. Abs., **18**, 2093).

tical and electrochemical methods is twice as soluble in N NaOH as red PbO. At lower temperatures red PbO is the more stable form. One judges they are talking about the red and yellow forms that exist below and above 650° as a result of an enantiotropic change, but this point is not clear in the abstract of the paper. When we heated the red or orange lead monoxide which appeared identical with the form commonly known as litharge, obtained by heating the hydrated lead oxide to 400°, in a nitrogen atmosphere to 650°, it changed to a yellow-colored solid. This change confirms the change Kohlschütter observed at 650° which he said was enantiotropic. The yellow color persisted when the material was cooled quite rapidly in the air and underwent no change in color over a two-week period. We infer the yellow material is in the metastable condition.

Some information as to what extent the lead oxide is decomposing the ethylene and by what means the reduction is accomplished is furnished by analysis of the gaseous products. A gas sample drawn off at 390° contained ethylene—87.5 percent, acteylene—0.0 percent, carbon dioxide—9.1 percent, carbon monoxide—2.1 percent, hydrogen—0.5 percent, methane, ethane—trace. These constituents in these amounts indicate only a relatively small decomposition of the ethylene and a reduction of the lead oxide carried out in such a way that carbon from the ethylene is oxydizid to carbon monoxide and carbon dioxide, mostly to the latter, and hydrogen to water. There is practically no splitting of the ethylene into: CH_2 groups or hydrogenation to ethane at this temperature. The main reaction is a chemical one between the lead oxide and the ethylene whereby reduction of the metallic oxide is accomplished. It is conceivable that carbon monoxide is a primary product which in turn is oxidized to the dioxide by more unreduced lead oxide. At any rate we may say that lead oxide does not activate ethylene catalytically under our experimental conditions and its presence in the composition of the glass tube as lead oxide alone is not contributing to the catalytic action of the tube.

The substances that go to make up the composition of Jena glass tubing, except aluminum oxide—6.3 percent, calcium oxide—0.08 perdent, sodium oxide—7.38 percent, K_2O—trace, and MnO—trace, have been separately studied to determine their activation of ethylene. Engelder has shown that aluminum oxide is inert toward ethylene. We have found that small amounts of sodium hydroxide mixed with silica are inactive. That leaves calcium oxide, present to the extent of 0.08 percent, and K_2O and MnO said to exist in Jena glass only in a trace, unaccounted for and of course any number of combinations in all proportions of these different oxide substances either as mixtures or definite compounds which might be run empirically, assuming that by chance there might be found a mixture favorable for ploymerizing ethylene. Before attacking this trial and error task, seeming unfruitful of immediate results, we shall turn our study to the action of certain metals.

The Action of Certain Metals on Ethylene

It has been known that metals like nickel, platinum, copper, aluminum, and magnesium decompose ethylene to varying degrees depending on the

temperature and condition of the metal. By the light of these observations and more recent cases such as Fischer's (loc. cit.) synthetic petroleum process where metallic substances have been effective we are led to study what effect on ethylene certain other metals may have.

Sodium as a Catalyst

This promoter of the polymerization of isoprene and butadiene ought to have some activity toward simpler hydrocarbons.

The metallic sodium was prepared for the experiments by filling a tube which would fit into the reaction tube and which contained a nitrogen atmosphere with sodium thread 1 mm. in diameter. The thread was obtained by forcing the soft metal through a sodium-press into the tube. The sodium-tube with the entrapped nitrogen was placed in the heating tube, already air-free, and containing a stream of oxygen-free ethylene at room temperature.

Table VIII shows what happens at different temperatures with sodium acting as a catalyst. The sodium melts at about 98° and agglomerates so that there is no advantage in the increased surface of the sodium thread except as a means of cutting the sodium for the reaction tube out of contact with air. If the reaction tube be held in a horizontal position the molten sodium remains in position in the center of the heating unit and can be heated in the ethylene atmosphere to 600° without danger. At 150° a colorless oil, assumed to be polymerized ethylene, condensed in very small amounts on the walls of the cooler part of the tube. The unsatisfied bonds between the carbon atoms were opened up:

$$x\left(\begin{matrix} H & H \\ | & | \\ H-C & :C-H \end{matrix}\right) = (C_2\dot{H}_4)x.$$

At the same time the oily liquid was forming, the sodium turned white. A white brittle solid was formed—sodium ethylene carbide and the condensation of colorless oil decreases. Finally all the sodium is converted to this new brittle material which has no reaction with ethylene and the polymerization stops. The gaseous products throughout this reaction contain no hydrogen or acetylene, Catalyst B and C, Table VIII at temperatures 165 and 150°.

If the sodium be heated to 200°, it begins to decompose the ethylene as well as to polymerize it—

$$\begin{matrix} H & H \\ | & | \\ H-C & :C-H \end{matrix} = C_2H_2 + H_2,$$

into acetylene and hydrogen. The acetylene is capable of uniting with metallic sodium and forms sodium acetylene carbide[1] or sodium acetylene,[2] C_2HNa. According to the investigators working with sodium acetylene this material decomposes at 210° into disodium acetylene and acetylene:

$$2C_2HNa = C_2Na_2 + C_2H_2.$$

At 200° molten sodium begins to absorb hydrogen which combines with the sodium to produce sodium hydride. Above 200° the colorless oil continues to

[1] Berthelot: Compt. rend., **62**, 455 (1866).
[2] Erdmann and Koethner: Z. anorg. Chem., **18**, 48. (1898).

condense in very minute quantities in the tube, the carbides appear as white masses and as grey and black material due to the presence of carbon as an impurity. At temperatures higher than 200° decomposition by splitting off hydrogen from the intermediate acetylene to leave carbon is taking place:

$$\begin{matrix} H & H \\ | & | \\ C & C \end{matrix} = 2C + H_2.$$

The vapor pressure of the molten sodium is sufficiently high at 400° to allow the sodium to distill over and condense beyond the heating unit on the walls of the tube in small amounts.

At 450, 500, and 550° the decomposition into acetylene and hydrogen according to:

$$\begin{matrix} H & H \\ | & | \\ H - C & C - H \end{matrix} = C_2H_2 + H_2$$

is increasing markedly, so that at 550°, Catalyst B, Table VIII, 64.7 percent of the ethylene is decomposed. The low acetylene yield at this temperature is accounted for on the basis of an interaction of the sodium and acetylene to form the acetylides and decomposition of the unstable acetylene into carbon and hydrogen. The presence of small quantities of methane indicates some

TABLE VIII
Ethylene over sodium.

Catalyst	A		B		
Temp. of tube (deg. C.)	100-240	240-470	165	500	550
Duration of run (in min.)	——	——	50	35	33
Cc. gas passed through	——	——	1060	620	420
Cc. gas evolved	——	——	1050	760	635
Cc. gas per min.	——	——	21.0	22.0	12.7
Percent C_2H_4 before	98.0	98.0	98.0	98.0	98.0
Percent C_2H_4 after	91.8	71.6	98.5	48.8	34.6
Percent decomposition	6.3	27.0	0.0	50.5	64.7
Analysis of gas:					
Ethylene	91.8	71.6	98.5	48.8	34.6
Acetylene	6.2	8.3	——	0.0	5.4
Hydrogen	1.3	9.8	——	43.4	46.1
Methane	——	trace	——	3.8	3.0
Ethane	——	trace	——	3.1	3.0
Total	99.3	99.8	98.5	99.1	99.1

splitting of the ethylene or acetylene between the carbon atoms into $:CH_2$ or :CH groups which are subsequently hydrogenated. Some ethylene is hydrogenated to yield the ethane present.

In brief it may be said that liquid sodium at 150° polymerizes ethylene to a colorless liquid and is itself at the same time changed to a white brittle mass of sodium ethylene carbide which is inert toward ethylene. At higher temperatures the polymerization continues along with a decomposition into hydrogen and acetylene, the latter in turn partly breaking down into carbon and hydrogen. The hydrogen forms hydrides with the sodium and acetylene forms acetylides and carbides. There is a small yield of methane indicative of a split between the carbon atoms of the ethylene or acetylene.

TABLE VIII A

Ethylene over sodium

Catalyst	C	D	
Temp. of tube (deg. C.)	150	400	450
Duration of run (in min.)	37	53	45
Cc. gas passed through	575	660	525
Cc. gas evolved	580	720	580
Cc. gas per min.	15.7	13.5	13.0
Percent C_2H_4 before	98.4	98.0	98.0
Percent C_2H_4 after	99.2	82.0	82.0
Percent decomposition	0.0	16.4	16.4
Analysis of gas:			
Ethylene	99.2	82.0	82.0
Acetylene	——	2.5	1.7
Hydrogen	——	13.1	12.0
Methane	——	1.1	2.0
Ethane	——	trace	trace
Total	99.2	98.7	97.7

Nickel as a Catalyst

Sabatier, we have been reminded, found that ethylene in contact with nickel decomposed into carbon and hydrogen and the latter was taken up at once by a portion of the ethylene to form ethane which was more and more broken down into methane at higher temperatures.

Preparation: 20 g. of Kahlbaum's C. P. nickel nitrate were dissolved in 120 cc. distilled water and 20 g. granulated pumice stirred in. The mixture was evaporated to dryness and then heated to dull redness until no more fumes of NO_2 were evolved, stirring frequently. Finely a strong blast-lamp flame was applied to drive off the last traces of nitric oxide. The pumice coated with nickel oxide was placed in the reaction tube where the catalyst was to be used and reduced at 350° by hydrogen for three hours.

Some preliminary runs using this nickel on pumice showed that up to 400° no polymerization took place, but considerable decomposition was going on

and only little ethylene survived. Finely divided carbon was deposited on the nickel and walls of the reaction tube. The gaseous products consisted of ethylene, acetylene, methane, ethane, and hydrogen. The action of the nickel on the ethylene was to split off hydrogen atoms to yield acetylene from which in turn more hydrogen was eliminated to produce the carbon. At the same time molecules of ethylene or acetylene separated between the carbon atoms to give $:CH_2$ or $\vdots CH$ groups which became hydrogenated to methane. It is known that finely divided nickel is the most active hydrogenation catalyst and there is nothing unusual about the fact that methane and ethane are formed, the latter of course as we have seen before by the hydrogenation of a part of the undecomposed ethylene.

Cobalt as Catalyst

Sabatier reported that with cobalt at 360° ethylene underwent slow carbonization without rapid swelling and much ethylene survived; that cobalt acted less actively than nickel. We repeated this experiment because Sabatier had run carbon monoxide and hydrogen over nickel and cobalt to get methane and Fischer runs a mixture of the same gases, according to his report, over cobalt and iron and obtains his petroleum and solid paraffins.

Preparation: Carried out as for nickel using cobalt nitrate in place of nickel nitrate and accomplishing the reduction of hydrogen at 515°.

A slow stream of ethylene was started through the apparatus as the heating current was turned on and the furnace allowed to heat up gradually from room temperature. Up to 545° no condensation of any polymerized ethylene as an oily liquid occurred, but much carbon had collected in the tube as evidence of considerable decomposition. Table IX shows to what extent the decomposition did take place and the gaseous products which thereby resulted. The same sample of catalyst was used for both the runs cited in the table. The above data are sufficient to show that a large part of ethylene is decomposed when in contact with finely divided cobalt at 400°. The principal products are hydrogen and carbon. No acetylene survives because it is more unstable than ethylene under the experimental conditions and breaks down into carbon and hydrogen as soon as it is formed from the ethylene. At this temperature the elimination of hydrogen from the ethylene and then from the intermediate acetylene seems to be the only manner in which ethylene is breaking down. Methane is found in just a trace. The ethane is a hydrogenation product.

Above 500° at 545° we are getting practically complete decomposition. The decomposition with this degree of heating takes place mostly by the separation of hydrogen from the carbon atoms which are left to form an amorphous carbon residue. The methane content of the gas product is 13.0 percent—a relatively large increase over the trace at 400°, which must mean a split in the molecules of ethylene or intermediate acetylene between carbon atoms so that $:CH_2$ or $\vdots CH$ groups can be furnished for hydrogenation to methane. It is apparently easier to split off hydrogen than to divide or separate the carbon atoms. It will be observed that the ethane content is perceptibly lowered. This means either that at this higher temperature ethane is

unstable and breaks down into carbon and hydrogen or $:CH_3$ groups or the deposition of the carbon on the cobalt is rendering the cobalt inert as a hydrogenation catalyst. The methane formation tends to disprove the latter. The actual behavior of the ethane could be ascertained by passing it alone over the cobalt at this same temperature, but Sabatier tells us that ethane is broken down at higher temperatures.

TABLE IX

Ethylene over cobalt

Catalyst	Finely divided cobalt		Cobalt plus 10 percent KOH
Temperature of furnace (deg. C.)	400	545	400
Duration of run in min.	28	20	38
Cc. gas passed through	525	460	700
Cc. gas evolved	560	720	800
Cc. gas per minute	18.7	23.0	18.4
Percent C_2H_4 before	98.5	98.5	98.5
Percent C_2H_4 after	58.6	2.7	33.1
Percent decomposition	40.5	97.4	66.4
Condensation of oil	nil	nil	nil
Deposition of carbon	large	larger	large
Analysis of gas:			
Ethylene	58.6	2.7	33.1
Acetylene	0.0	0.0	0.0
Hydrogen	33.5	82.7	46.8
Methane	trace	13.0	6.9
Ethane	6.4	1.9	11.5
Total	98.5	100.5	98.3

Table X gives observations for various increasing temperatures which substantiate previous observances that cobalt does not tend to polymerize ethylene into liquid hydrocarbons.

TABLE X

Cobalt oxide reduced at 440°.

Ethylene over cobalt at rate of one liter per hour.

Time	Potentiometer reading in millivolts	Temperature equivalent	Condensation of oil
4 : 20	9.3	225	nil
: 32	12.6	305	"
: 48	15.5	375	"
5 : 00	17.0	415	"
: 21	23.5	565	"

Sufficient KOH to make 10 percent by weight on the metallic cobalt basis was added to cobalt oxide on pumice, dissolved in water added to the mixture, and the mixture evaporated to dryness. There resulted KOH distributed over the cobalt oxide which rendered the subsequent cobalt alkaline after reduction. The ethylene in a slow stream passing over this alkalized cobalt catalyst showed no tendency to form liquid products up to 550°. No condensation of oils took place, but much carbon collected over the surface of the catalyst filling the tube. Table IX gives the results of a gas analysis of the products collected at 400° and indicates the extent of the decomposition. Apparently the KOH has increased the activity of the cobalt for less ethylene survives than at the same temperature and with the same rate of gas flow with pure cobalt. In addition to eliminating hydrogen, $:CH_2$ or $\vdots CH$ groups are produced which hydrogenate to yield methane. Before it can become established that the alkali has increased the activity of the cobalt further study is needed to make certain the temperatures are identical as recorded and that the rate of gas flow is kept uniform throughout the run, for a slower flow would increase the decomposition decidedly. More attention will be paid to the function of the alkali in the case of iron.

Iron as a Catalyst

Preparation: 20 g. of ferric nitrate (C.P.) were dissolved in 120 cc. distilled water and 20 g. granulated pumice stirred in. The mixture was evaporated to dryness and then heated to dull redness until no more fumes of NO_2 were evolved, stirring frequently. Finally a strong blast-lamp flame was applied to drive off the last traces of nitric oxide, leaving a layer of red-brown oxide on the pumice. As required for use, the oxide coated pumice was placed in position in the reaction tube and reduced by hydrogen at different temperatures.

TABLE XI

Catalyst A.
Ethylene over iron reduced at 350°.
Rate of gas flow—one liter per hour.
Tube and catalyst heated from room temperature.

Time	Potentiometer readings in millivolts	Temperature equivalent in deg. C.	Condensation of oil	Change in iron
10 : 36	9.5	230	nil	nil
: 45	12.8	310	"	"
: 49	14.0	340	"	"
11 : 24	15.5	375	colorless oil	"
: 43	15.5	375	colorless oil	apparently none
3 : 18	17.5	425	light brown and colorless oil	carbon depositing

Carbon sufficient at 425° to fill tube and prevent gas flow.

Some typical results of passing ethylene in a slow stream of one liter per hour over the heated iron catalyst are recorded in Table XI.

Here is a catalyst which is approaching the accomplishment with ethylene which we have been seeking among the various catalytic substances. Without question the finely divided iron on pumice is opening up the unsatisfied bonds between the carbon atoms of ethylene to allow the ethylene molecules to join together to form a liquid polymer. The iron begins to do this at about 360°.

TABLE XII

Catalyst B.

Ethylene over iron reduced at 330°.

Rate of gas flow—one liter per hour.

Tube and catalyst heated from room temperature.

Time	Potentiometer readings in millivolts	Temperature equivalent in deg. C.	Condensation of oil	Change in iron
1 : 44	13.50	330	nil	nil
: 57	14.50	353	"	"
2 : 00	14.70	358	colorless oil in min. amt.	"
: 10	15.50	375	colorless oil in min. amt.	"
5 : 15	15.00	365	colorless oil in min. amt.	carbon at first contact with catalyst

TABLE XIII

Ethylene over iron catalysts A and B.

Catalyst	A	B
Temperature in deg. C.	425	365
Duration of run in min.	——	55
Cc. gas passed through	——	630
Cc. gas evolved	——	800
Cc. gas per minute	——	11.4
Percent C_2H_4 before	98.5	98.5
Percent C_2H_4 after	3.3	40.1
Percent decomposition	98.7	59.3
Analysis of gas:		
Ethylene	3.3	40.1
Acetylene	0.0	2.4
Hydrogen	49.8	40.7
Methane	40.5	3.6
Ethane	5.8	10.4
Total	99.4	97.2

Unfortunately, but as might be expected, the iron at the same time is bringing about decomposition as well as polymerization and carbon, detrimental to the continuous activity of the iron for the formation of the liquid products, is produced. As Table XII indicates, after three hours contact of the ethylene at 365° carbon has collected in sufficient amount on the iron to become plainly visible. The analysis of the gaseous products coming off at this temperature reveals a large decomposition, 60 percent, principally into carbon and hydrogen, Table XIII. If the temperature be lowered sufficiently to prevent this deposition of inert carbon the condensation of the colorless oil ceases. The presence of methane indicates a splitting between carbon atoms as well as elimination of hydrogen.

A comparison of the action of iron with that of cobalt from the data given herein is hardly fair because the ethylene remained much longer in contact with the iron than with the cobalt, thereby giving opportunity for decomposition to go more nearly to completion. It seems reasonable to say, however, that ethylene is more unstable toward iron than toward cobalt and that the iron is promoting to a far greater extent than cobalt the decomposition of ethylene whereby $:CH_2$ groups are produced for ultimate hydrogenation to methane.

At 425° the carbon deposition was voluminous enough to completely fill the tube and to stop the passage of gas under the pressure ordinarily obtained from the water-head. Added air pressure forced sufficient gas through the reaction tube to evolve the gas required for an analysis. Under these conditions the ethylene was almost entirely broken down into carbon and hydrogen and methane. It is interesting to note the great readiness with which the iron separates the carbon atoms to split off $:CH_2$ groups, yielding the resultant 40.5 percent methane, a very large increase over the 3.6 percent methane obtained at 365° and considerably more than cobalt gave at 545°, although we must still bear in mind the faster rate of gas flow when using cobalt. Also we find the ethane content of the gaseous products lower at the higher temperature which is due to the unstability of the ethane at the higher temperature

The yield of liquid hydrocarbons as a colorless oil is small. Only a fraction of a cc. can be obtained before the catalyst is rendered inert by carbon deposition. This very small yield is temporarily considered encouraging inasmuch as we have not found thus far any other single substance or mixture of substances which will accomplish the polymerization of ethylene at as low a temperature. Further, it should be possible to increase the condensation of liquid polymers by applying pressure to the system and at the same time reduce, if not entirely eliminate, the decomposition which results in an increase of gas volume. For the purpose of trying to get a continuous and quantitative condensation of the liquid products we shall later employ a pressure apparatus which will enable us to study this activity of the iron at 20 to 30 atmospheres pressure.

Weakly Alkalized Iron as Catalyst

To 20 g. ferric nitrate, 20 g. granulated pumice, 0.023 g. KOH, and 150 cc. distilled water were added and the mixture treated as ferric nitrate alone without the alkali. The reduction by hydrogen was carried out at 400°. This quantity of KOH was the amount calculated to give 1 percent KOH by weight on the basis of the quantity of iron finally coating the pumice. With such a catalyst condensation of a colorless oil occurred only after a temperature above 400° was reached and the yield of oil was very minute—less than with iron alone. Simultaneously, decomposition was taking place as shown by carbon deposition.

Next the iron oxide was coated on the pumice as in preparing the metallic iron catalyst and to the oxide on pumice was added 0.02 g. KOH with distilled water to dissolve the alkali. The solution covering the oxide-pumice material was evaporated to dryness and the resulting mixture reduced in a hydrogen atmosphere at 365°. After passing a slow stream of ethylene over the alkalized iron prepared in this way and heating to 475° no condensation of any oil occurred, but decomposition of the ethylene had begun.

We do not pretend to have exhausted the possibilities of alkalized iron either in our methods of preparation or in the ratio of alkali to iron used. It is conceivable that higher percentages of alkali with the iron may be more effective in polymerizing the ethylene. The low proportion of alkali inhibits the activity of the finely divided iron.

Iron and Chromium Oxide in Varying Proportions as Catalyst

Iron plus one percent chromium oxide.

Preparation: To 20 g. ferric nitrate ($Fe(NO_3)_3.9H_2O$) were added 20 g. granulated pumice, 0.14 g. chromium nitrate ($Cr(NO_3)_3.9H_2O$), and 150 cc. distilled water. Evaporated to dryness and calcined, whereby iron oxide and chromium oxide were left distributed over the pumice. This quantity of chromium nitrate was sufficient to yield one percent chromium oxide by weight on the basis of the iron finally obtained after reduction. Reduction was carried out with hydrogen over night at 520°.

When the ethylene passed over this iron and one percent chromium oxide on pumice at 390° it underwent polymerization to a small extent and at the same time decomposition. Very minute quantities of colorless oil condensed in less amounts than with iron alone. Deposition of carbon and increase of pressure at 395° measured by an attached manometer indicated decomposition. Below 390° no condensation occurred and there was no carbon deposited on the iron. The chromium oxide partly destroys the catalytic action of the iron which additional runs using 10 percent and 100 percent chromium oxide show more clearly.

Iron plus 10 Percent Chromium Oxide

Prepared as the 1 percent mixture using 1.4 g. chromium nitrate in place of the 0.14 g. Reduction by hydrogen carried on at 525°. With this mixture of higher chromium oxide content no condensation at all took place at 390°, and none even at 480° where carbon was being deposited on the catalyst. 10

percent chromium oxide, under our experimental conditions, prevents entirely the iron activation of ethylene whereby the unsatisfied bonds between the carbon atoms are opened up for polymerization.

Iron plus 100 Percent Chromium Oxide

For this catalyst 14 g. of chromium nitrate were weighed out with the ferric nitrate and pumice. Reduction by hydrogen took place at 460°. Such a mixed material of iron and 100 percent chromium oxide remained inert toward ethylene below 500°. The ethylene at this temperature underwent decomposition and no indication of polymerization is observed throughout the heating range from room temperature. Chromium oxide is not a promoter of the polymerization of ethylene by iron, but its presence decreases the surface of the iron in contact with the gas and inhibits the action which iron alone has.

Iron supported by Chromium Oxide as a Catalyst

20 g. Merck's anhydrous chromium oxide, 270 g. ferric nitrate and 350 cc. distilled water were stirred together and gently heated until the ferric nitrate entirely dissolved. The mixture of solution and chromium oxide was then evaporated to dryness and the dry mass calcined. A portion of the combined oxides of iron and chromium were reduced in position in the reaction tube at 460°, thus forming metallic finely divided iron on chromium oxide as a support. As far as polymerization of the ethylene is concerned chromium oxide makes a poorer support than pumice because it exposes less surface and is itself inert.

TABLE XIV

Ethylene over iron supported by chromium oxide.

Time	*Potentiometer* readings in millivolts	Temperature equivalent in deg. C.	Condensation of oil
10 : 47	9.0	220	nil
: 52	11.0	265	"
11 : 11	15.0	365	"
: 20	16.0	390	"
: 26	17.5	425	"
: 38	20.0	480	"

Table XIV indicates that chromium oxide as a carrier for the catalytic iron is not as good as granulated pumice. We had hoped the iron might at least retain on chromium oxide the activity it possessed when supported by the pumice, but the oxide does not present the surface the porous pumice does and the finely divided oxide may be coating some of the metallic iron surface. It was proposed to use the chromium oxide carrier for weakly alkalized iron catalyst since when on pumice the fused alkali was interacting to yield a silicate and the potassium hydroxide did not remain present as such. A sample of iron, plus 1 percent KOH, supported by the chromium oxide was run and no condensation of any colorless oil or liquid products appeared up through 425°.

Iron under Pressure as Catalyst

Apparatus: The apparatus as set up for working conditions under pressure is shown in Fig. 2. The 25 lb. ethylene gas tank E is connected by a series of heavy brass fittings to an inch and a quarter steel tube P (internal diameter 3/4″), four feet long. G is a 500 lb. steam pressure gauge and V_1 a needle-valve for the hydrogen intake for reduction in preparing the iron catalyst. The steel reaction chamber P is heated by chromel resistance wire wound around the thermocouple protection tube as well as the steel tube itself. Insulation is secured by a 3″ thick covering of air-cell asbestos. Tightness at

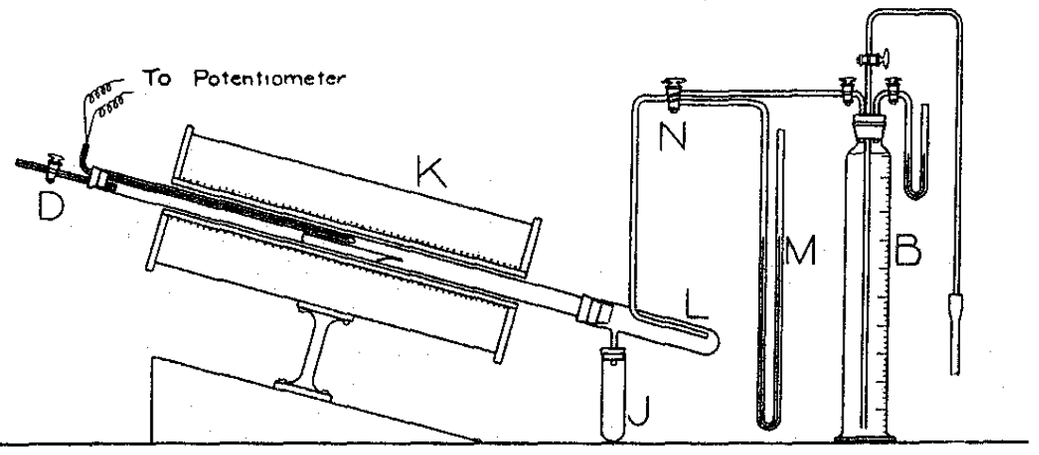


FIG. 2

the bolted joints shown in the sketch is secured by pressure of the steel tube-end against a lead seat. Valve V_2 regulates the flow of gas from the tube and ethylene tank valve is set correspondingly to maintain constant pressure. The condenser C is immersed in a brine bath, from which the gases evolved escape into the collecting cylinder B. R is a receiver for any liquid products. O is the outlet for the salt solution used as the confining liquid in B.

Procedure: Catalyst A in Table XV was prepared by mixing 40 g. ferric nitrate dissolved in 200 cc. distilled water and 40 g. granulated pumice, evaporating the aqueous mixture to dryness, and calcining as done previously. The ferric oxide-coated pumice was placed for a 75 cm. length of the middle portion in the reaction tube and reduced by hydrogen at 400° for eight hours. The apparatus was cooled to room temperature, keeping a slow stream of hydrogen passing through the tube. The needle-valve to the hydrogen tank was then closed and ethylene run in to displace the hydrogen. The heating current was turned on, the pressure increased and maintained at 10 atmospheres, and the reaction chamber heated slowly to 365°. According to the gas analysis of two samples collected at different rates of flow, viz 5.75 and 3.10 liters per hour, no decomposition of the ethylene took place. No liquid products condensed in the cooler part of the tube. Now the temperature was raised to 430° and the pressure increased to 20 atmospheres. Under these conditions the ethylene did decompose to the extent of about 4 percent. The gases other than ethylene evolved were 0.9 percent hydrogen and 2.6 percent ethane. An ex-

amination of the catalyst after completing the run revealed the presence of carbon deposited in a thin film over the iron-covered granules of pumice.

Catalyst B was similarly prepared, being reduced in an hydrogen atmosphere at 400° for eight hours. Under a pressure of 20 atmospheres the temperature of the ethylene passing through the tube was increased from room temperature to 365° and held constant throughout the time of taking a sample of the gaseous products for analysis. As a consequence of the lower rate of gas flow and longer contact of the ethylene with the iron less ethylene survived than with faster rates of flow. We note that the gaseous products contained no acethylene and no methane, very little or practically no hydrogen and a considerable increase of ethane relative to the previous run at a higher temperature. When the iron on the pumice was removed from the tube it was found that a film of carbon had formed on the grains of pumice. As long as carbon became deposited on the catalyst to render it inert no liquid products would have a chance to form in amounts which would be appreciable, so the temperature was lowered to eliminate the decomposition whereby carbon is formed. At the same time the pressure on new catalytic material was increased further to promote polymerization.

TABLE XV

Ethylene over finely divided iron as catalyst under 10, 20, 30, atmospheres pressure.

Catalyst		A		B	C	
Temp. of tube (deg. C.)	365	365	430	365	340	340
Pressure of gas (in atm.)	10	10	20	20	30	30
Duration of run, in min.	12	21	24	71	14	34
Cc. gas evolved	1150	1035	1300	1080	750	490
Rate per hour (in liters)	5.75	3.1	3.25	.91	3.2	.86
Percent C_2H_4 before	99.0	99.0	99.0	99.0	99.0	99.0
Percent C_2H_4 after	99.0	99.5	95.4	83.2	99.2	98.9
Present decomposition	00.0	00.0	3.6	17.0	00.0	00.0
Condensation of oil	Inappreciable					
Deposition of carbon	small amt. on iron			carbon film	catalyst coated	
Analysis of gas:						
Ethylene	99.0	99.5	95.4	83.2	99.2	98.9
Acetylene	——	——	——	——	——	——
Hydrogen	——	——	0.9	0.7	——	0.2
Methane	——	——	——	——	——	——
Ethane	——	——	2.6	15.0	——	——
Total	99.0	99.5	98.9	98.9	99.2	99.1

Catalyst C, freshly prepared as A and B, was reduced four hours in a hydrogen atmosphere at 400°. Ethylene was passed over the finely divided iron under 30 atmospheres pressure at a temperature of 340° for two and a half

hours. As the results of analysis of two samples collcted during this interval show, approximately no decomposition was taking place nor was any appreciable amount of oily products formed. The catalyst when removed from the reaction chamber possessed a deposit of carbon sufficient to rub off on the hand. The small amount of ethane formed simultaneously with the carbon escaped detection, but a trace of hydrogen was found. The accumulation, of the free carbon was sufficient to destroy the activity of the iron.

If the ethylene be decomposing so that hydrogen is split off and acetylene produced in a manner such as:

$$\begin{array}{c} H\ \ H \\ \text{------}|\text{---}|\text{------} \\ H - C : C - H \end{array} = C_2H_2 + H_2,$$

increased pressure would tend to decrease the reaction. The hydrogen as soon as it is formed, however, unites with another portion of the ethylene to yield ethane and the net result is a change involving no alteration in volume, being characteristic of the catalyst alone.

$$_2C_2H_4 = C_2H_6 + C_2H_2.$$

In turn, as we have found above, the acetylene breaks down into carbon and hydrogen because it is more unstable than the ethylene and pressure has no influence upon decomposition accompanied by no volume change. The hydrogen thus produced does not remain uncombined because the hydrogenation of ethylene to ethane is promoted by increasing the pressure.

The dissolution of the bonds between the carbon atoms to form $:CH_2$ groups is entirely prevented by the increased pressure, since there is an increase in volume when $_2$ $:CH_2$ groups are produced from ethylene. Under the high pressure conditions if methane were formed it must result by such a reaction as:

$$C_2H_4 = C + CH_4,$$

in which the ethylene is unsymmetrically broken down. Because no traces of methane can be found in the gases evolved the ethylene cannot be decomposing this way under the influence of the iron catalyst. At atmosheric pressure where methane does form in large quantities it must be produced by subsequent hydrogenation of $:CH_2$ groups into which the ethylene molucules have been split. Thus we establish the manner in which methane is formed by the decomposition of ethylene and it is reasonable to assume that the same method applies for acetylene.

Undoubtly increased pressure does promote the polymerization of ethylene to liquid hydrocarbons, but pressure cannot prevent the formation of carbon from ethylene in contact with iron and the simultaneous formation of the carbon film on the catalyst by which the latter is made inert. This decomposition of ethylene into carbon is promoted by the catalyst and remains unaffected by increasing the pressure.

General Conclusions

The general conclusions to be drawn from this paper are:

1. Ethylene is stable toward heat under the conditions of our experiment until the temperature exceeds 600°. Above this temperature in the Jena glass reaction-tube the gas polymerizes to a colorless and brown oil and at the same time decomposes into acetylene, hydrogen, methane, and carbon and hydrogenates to ethane.

2. A possible mechanism for the formation of these various products and succeeding products is given.

3. The thermal decomposition of acetylene has been studied for comparison with that of ethylene and it has been found that acetylene is stable toward heat up to 400°, above which it tends to polymerize to a brown fluorescent liquid, to decompse to a small extent into carbon, hydrogen, and methane, and to hydrogenate to ethylene.

4. The liquid obtained by passing a mixture of equal parts of acetylene and ethylene at 600° through an empty Jena tube is a mixture of polymerized acetylene and polymerized ethylene.

5. An attempt to find out what it is in the Jena glass which catalyzes the polymerization of ethylene and acetylene by running each constituent of the glass separately and in a finely divided state has been unsuccessful.

6. The activation of the ethylene by the walls of the reaction chamber is thought to be due to a combination of two or more of the oxide constituents which come into play at the elevated temperature.

7. Silica gel, silica gel and borax, silica gel and calcium hydroxide, calcium hydroxide, borax, calcium silicate, and zinc oxide are insert toward ethylene up to 600°.

8. Ethylene reacts with ferric oxide and reduces it completely at 500°.

9. Ethylene reduces zinc oxide completely at 800-900°.

10. Ethylene reduces lead monoxide completely at 600°.

11. The two yellow forms and the red-orange (litharge) form of lead monoxide have been worked with and an attempt to account for their occurrence made in the light of previous work with similar material.

12. The action of molten sodium on ethylene through a temperature range from 100° to 550° has been studied. Throughout this range the ethylene is polymerized to a colorless oil; the sodium reacts with the ethylene and decomposition product, acetylene, to form carbides and with the liberated hydrogen to produce hydrides; the ethylene undergoes a decomposition to hydrogen, carbon, and methane; a small undecomposed portion is hydrogenated to ethane.

13. Only a small amount of ethylene survives after passage over nickel at 400°. No polymerization takes place. The decomposition products are hydrogen and acetylene, the latter in turn breaking down into carbon and hydrogen, and some methane as a result of a split between the carbon atoms to yield : CH_2 groups which are hydrogenated to methane.

14. In contact with cobalt ethylene undergoes rapid carbonization at 400° and is completely decomposed at 545°. No liquid polymers are formed.

15. Iron polymerizes ethylene at 360° to a colorless oil and at the same time decomposes the hydrocarbons slowly to hydrogen and carbon. At 425° decompsoition is practically complete and results as a dissolution of the carbon atoms bonds to yield : CH_2 groups to a large extent. Being a fairly good hydrogenating catalyst the ethane content of the gaseous products is comparatively high.

16. Iron weakly alkalized with potassium hydroxide, as far as we have studied, is no improvement over finely divided iron itself for accomplishing the polymerization of ethylene.

17. Chromium oxide mixed with metallic iron is not a promoter of the activity of iron.

18. Chromium oxide serves as a poorer support for the iron catalyst than granulated pumice because it does not prevent the surface porous pumice possess and it coats the metallic iron surface.

19. In pressure studies the actual way in which methane is produced from ethylene is found to be by splitting of the molecule between the carbon atoms to yield 2 : CH_2 groups which are subsequently hydrogenated to methane.

20. Increased pressure does not establish a condition for a continuous formation of liquid polymers of ethylene because the iron catalyst decomposes ethylene into inert carbon which poisons the catalyst independent of pressure.

Acknowledgments

The author welcomes this opportunity to express his gratitude to Professor Wilder D. Bancroft at whose suggestion and under whose direction this investigation was undertaken. I am most indebted to him for his kindly interest, helpful critism, valuable suggestions, and encouragement throughout the progress of the work. I can express too inadequately my thanks for Professor Bancroft's generosity and for the inspiration of association with him.

As a recipient of the Augustus Howe Buck Fellowship from the Augustus Howe Buck Educational Fund in Boston University for the years 1924-1927 the writer is deeply grateful to the doner for the generous Fellowship and for the opportunity for including this Graduate work and to the Committee that awarded it.

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Cornell University

1-120

STUDIES IN ADSORPTION. XIX

Adsorption of electrolytes by manganese dioxide, and a discussion of the Freundlich adsorption formula

BY M. N. CHAKRAVARTI AND N. R. DHAR

Introduction

In previous papers[1] published from these laboratories it has been proved that the phenomenon of adsorption is more marked when there is some sort of chemical affinity between the adsorbent and the substance to be adsorbed. Moreover it has been shown that those substances which can form complex salts with the adsorbent are likely to be adsorbed in large quantities.

It has also been proved that a freshly precipitated substance can be peptised by a reagent which in excess exerts a solvent action on it, and forms a complex ion with it. Peptisation can also take place when the freshly precipitated substance is brought in contact with a reagent which can dissolve a substance forming simple ions. The first stage in the formation of a complex ion is the formation of a sol or a coarse suspension of the material which is being dissolved forming a complex ion.

In this paper, we shall bring forward further evidence in support of the chemical view of adsorption and sol formation.

Recently there has been some discussion with regard to the interpretation of the Schulze-Hardy law when applied to adsorption experiments[2]. We shall first state the facts and bring out the point of dispute as clearly as possible. (1) From experiments on the coagulation of many sols with different electrolytes, it is now established at least qualitatively that the greater the valency of the oppositely charged ions the greater is its coagulating power. This is really what is known as the Schulze-Hardy law, and this deduction is quite sound as it is based on experiments.

(2) Several workers in this field, notably Bancroft[3], Weiser[4], and others have tacitly assumed that the greater the adsorbability of an ion the greater would be its coagulating power.

We shall show that this assumption has very little experimental support even in the adsorption of ions of the same valency, not to speak of ions of different valencies.

Combining this second assumption, which is not yet experimentally proved, with the first deduction, which is experimentally sound, Weiser, Bancroft, and other workers in colloid chemistry, have come to the conclusion that an ion of higher valency, which has high coagulating power, is more adsorbed than an ion of lower valency, which has small coagulating power.

[1] Kolloid-Z., **35**, 144 (1924); J. Phys. Chem., **28**, 457 (1924).
[2] J. Phys. Chem., **29**, 955 (1925).
[3] J. Phys. Chem., **19**, 349 (1915).
[4] J. Phys. Chem., **29**, 955 (1925).

Experimental

In order to find out whether an ion of higher valency is adsorbed in greater quantities than ions of lower valency, we have undertaken a series of adsorption experiments with a pure sol of hydrated manganese dioxide. This was prepared by the interaction of a standard solution of $KMnO_4$ and H_2O_2 at the ordinary temperature[1]. The chemical change involved in the reaction is the following:—

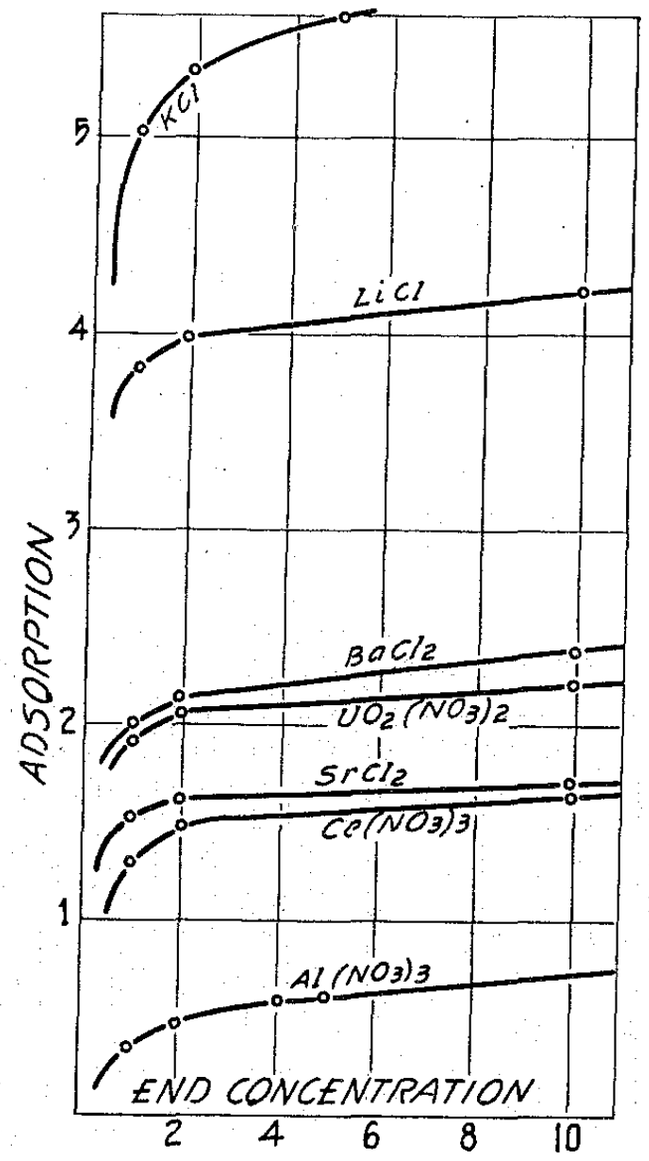


FIG. 1
Adsorption of cations by a sol of negatively charged MnO_2.

$$2KMnO_4 + H_2O_2 = 2MnO_2 + 2KOH + 2O_2.$$

This was dialysed for a week, until the sol was completely free from KOH or any excess of $KMnO_4$.

The concentration of the sol was determined both gravimetrically and volumetrically and the mean gave the concentration as 1.627 grams of MnO_2 per litre of the sol.

[1] Bredig and Marck: "Van Bemmelen Gedenkboek", 342 (1910).

A measured volume of the sol was taken in a dry glass-stoppered bottle and then 20 cc. of distilled water was put in and 10 cc. of M/10 solution of the electrolyte was then added. The bottle was stirred well and kept in the dark for about 20 hours and after the lapse of time the strength of the electrolyte in the supernatent liquid was estimated; from the difference between this and the initial concentration of the electrolyte, the amount of the electrolyte adsorbed was calculated, Tables I-II, and Figs. 1-2.

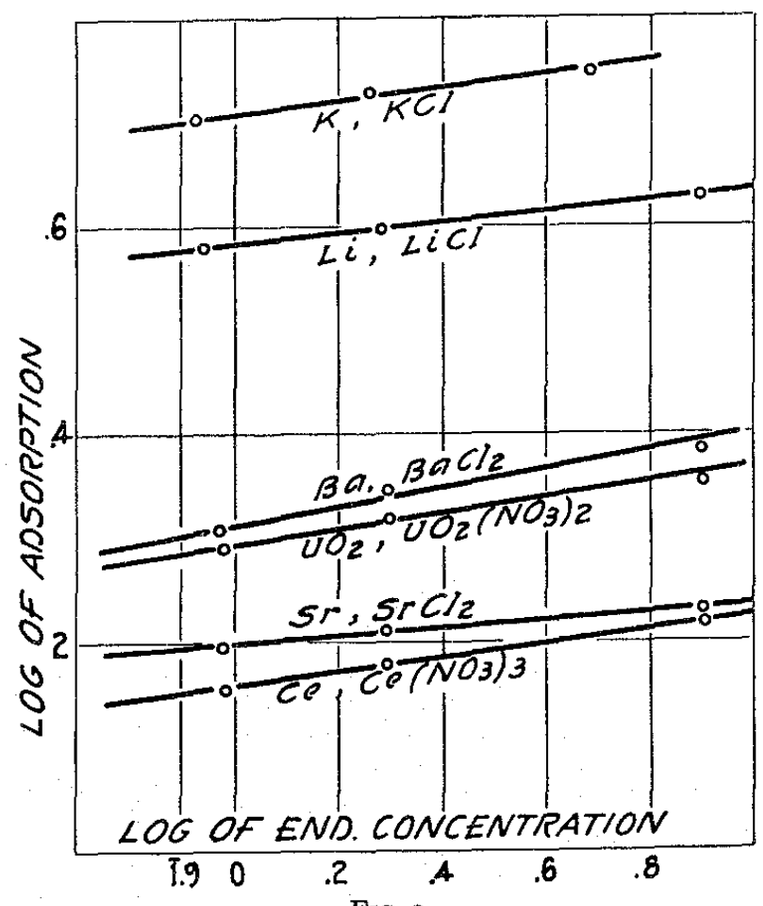


FIG. 2
Adsorption of cations by a sol of negatively charged MnO_2.

TABLE I

Strength of sol = 1.627 gms. per lit.; volume of sol used = 20 cc.; total volume = 50.0 cc.; time = 20 hours

Initial concentration in millimoles per 50 cc.	End conc. in millimoles per 50 cc.	Adsorption per gm. of MnO_2 in millimoles
	$AgNO_3$—Volumetrically with KCNS.	
1.00	0.8025	5.925
1.00	0.8025	5.925
1.00	0.8050	5.850
		Mean 5.900
	$CuCl_2$—Iodometrically.	
10.00	9.8300	5.100
5.00	4.8400	4.800
1.00	0.8680	3.860

TABLE I (continued)

Initial concentration in millimoles per 50 cc.	End conc. in millimoles per 50 cc.	Adsorption per gm. of MnO_2 in millimoles
$BaCl_2$—Gravimetrically as $BaSO_4$		
1.00	0.9354	1.938
1.00	0.9339	1.983
1.00	0.9337	1.989
	Mean	1.970
KCl—Gravimetrically as K_2SO_4.		
1.00	0.8155	5.535
1.00	0.8161	5.517
1.00	0.8162	5.514
	Mean	5.522
$CuSO_4$—Iodometrically.		
1.00	0.8691	3.927
1.00	0.8730	3.813
1.00	0.8668	3.996
	Mean	3.912
$Al(NO_3)_3$—Gravimetrically as Al_2O_3.		
1.00	0.9890	0.330
1.00	0.9880	0.360
1.00	0.9890	0.330
	Mean	0.340
$UO_2(NO_3)_2$—Volumetrically with phosphate.		
1.00	0.9350	1.950
$Ce(NO_3)_3$—Gravimetrically as CeO_2.		
1.00	0.9555	1.334
$SrCl_2$—Gravimetrically as $SrSO_4$.		
1.00	0.9481	1.559
LiCl—Gravimetrically as LiCl anhydrous		
1.00	0.8727	3.820
$Th(NO_3)_3$—Gravimetrically as ThO_2.		
1.00		Charge reversal.
$HgCl_2$—Volumetrically with KI.		
1.00		Insufficient to coagulate

TABLE II

Strength of sol = 1.627 gms. per lit.; volume of sol used = 20 cc.; total volume = 50 cc.; time = 20 hours

Initial concentration in millimoles per 50 cc.	End conc. in millimoles per 50 cc.	Adsorption per gm. of MnO_2 in millimoles
	$UO_2(NO_3)_2$—Volumetrically with phosphate.	
10.00	9.9250	2.250
2.00	1.9305	2.075
1.00	0.9350	1.950
	$BaCl_2$—Gravimetrically as $BaSO_4$.	
10.00	9.9200	2.400
2.00	1.9284	2.149
1.00	0.9295	2.015
	$Ce(NO_3)_3$—Gravimetrically as CeO_2.	
10.00	9.9450	1.650
2.00	1.9500	1.500
1.00	0.9555	1.334
	$SrCl_2$—Gravimetrically as $SrSO_4$.	
10.00	9.9440	1.680
2.00	1.9458	1.626
1.00	0.9481	1.559
	LiCl—Gravimetrically as LiCl anhydrous.	
10.00	9.8588	4.236
2.00	1.8682	3.954
1.00	0.8727	3.820
	$Th(NO_3)_4$—Gravimetrically as ThO_2.	
10.00 2.00 1.00	Charge reversal.	
	KCl—Gravimetrically as K_2SO_4.	
5.00	4.8126	5.622
2.00	1.8205	5.385
1.00	0.8330	5.010
	$HgCl_2$—Volumetrically with KI.	
10.00 2.00 1.00	Insufficient to coagulate.	

TABLE II (continued)

Initial concentration in millimoles per 50 cc.	End conc. in millimoles per 50 cc.	Adsorption per gm. of MnO_2 in millimoles
	$Al(NO_3)_3$—Gravimetrically as Al_2O_3.	
5.00	4.9793	0.621
2.00	1.9830	0.480
1.00	0.9887	0.340
	$Th(NO_3)_4$—Gravimetrically as ThO_2.	
0.0059	0.0050	0.03 approximately
	$CuSO_4$—Iodometrically.	
10.00	9.8230	5.310
2.00	1.8350	4.950
1.00	0.8729	3.996

From the foregoing results obtained with a pure sol of manganese dioxide, we can conclude that the higher the valency of the ion, the less is the adsorption. The order in which the ions were adsorbed is the following:—

$$Ag > K > Cu(CuSO_4) > Cu(CuCl_2) > Li > Ba > UO_2 > Sr > Ce > Al > Th.$$

This result is in direct opposition to the view held by Bancroft, Weiser and others, viz. that an ion of a higher valency is more adsorbed than an ion of a lower valency.

The experiments on coagulation of a sol of $Fe(OH)_3$, by Weiser and Middleton[1]; of $Al(OH)_3$ by Gann[2]; of HgS by Freundlich[3]; of Sb_2S_3 by Ghosh and Dhar[4]; are in support of our experiments, which give, that the greater the valency of an ion, the less is the adsorption.

On comparing the results of Freundlich, on the adsorption obtained with the sol, and with the powdered As_2S_3, we find that in general the adsorption of the same ion is greater with the sol than with the powder. This is, as is expected, and the difference is mainly due to the amount of the ion necessary to neutralise the charge of the sol. From the results on coagulation and adsorption by As_2S_3 sol, as well as by powdered As_2S_3, we find that in general an ion of a higher valency is adsorbed less, when the amount of adsorption is expressed in millimoles. In other words, the adsorptions when expressed in milliequivalent are equal, as has been first observed by Whitney and Ober[5]. There is nothing in the experiments with As_2S_3 sol, to show that the greater the valency of an ion the greater is the amount of its adsorption.

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[1] J. Phys. Chem., **24**, 30 (1920).
[2] Kolloidchem. Beihefte, **8**, 63 (1916).
[3] Z. physik. Chem., **85**, 641 (1913).
[4] J. Phys. Chem., **29**, 435 (1925).
[5] J. Am. Chem. Soc., **23**, 842 (1901).

From the researches of Sen[1], submitted in his thesis, one fact comes out very prominently, that $Fe(OH)_3$ is a much better adsorbent of acids and salts than As_2S_3. Moreover the large amount of adsorption of the acids is mainly due to the chemical affinity of ferric hydroxide for these acids. Though large amount of acid is adsorbed by precipitated $Fe(OH)_3$, it is useless to correlate this adsorption with the coagulating power of the electrolyte, because we are convinced that this high adsorption has nothing to do with the question of charge neutralisation of the sol, but is essentially due to the chemical affinity of ferric hydroxide for the acids. Moreover, it will be evident from the results of Weiser and Middleton[2] on the coagulation of a sol of Al $(OH)_3$, that this is a very good adsorbent for different ions, although Ishizaka[3] has shown that "grown alumina" can adsorb ions to the extent of only 0.002 to 0.050 millimoles per gram of the adsorbent.

In the case of aluminium hydroxide sol the amount of adsorption due to the chemical affinity is more pronounced than that due to charge neutralisation, because the precipitated $Al(OH)_3$ can adsorb large quantities of acids. The experiments of Sen on the adsorption of acids by freshly precipitated $Cr(OH)_3$, show that acids are very highly adsorbed by $Cr(OH)_3$ and its adsorptive power is greater than those of either $Fe(OH)_3$ or $Al(OH)_3$.

In this connection we have to emphasise that the adsorption of ions is much greater by a definite weight of the adsorbent in the course of its formation than that obtained, when the same weight of the adsorbent, prepared long ago, is used. It has been repeatedly observed that sols of $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$, MnO_2, etc., are much better adsorbents of ions than the precipitated substances. Moreover, the adsorbability and the chemical reactivity of ions decrease with the ageing of the precipitates. When a sol is precipitated by an electrolyte the neutralisation of the charge takes up a definite quantity of the oppositely charged ion, and if the neutral particles thus formed have a very slight chemical affinity for the coagulating ion, we should always find, that the adsorption of different ions, expressed in equivalents, should be practically equal, just as we get in the case of As_2S_3 sol to a certain extent.

When the adsorption is expressed in moles per gram of the adsorbent, has has been done in this paper, we ought to find that, in general, the greater the valency of an ion the less is its adsorption.

In the case of substances like the above hydroxides, MnO_2, etc., the chemical affinity of these substances for the coagulating ion is much more pronounced than in the case of the sulphides of arsenic and antimony. Consequently the correlation between the coagulating powers or the valency of the ions with their amounts of adsorption is less satisfactory than in the case of substances like As_2S_3 or Sb_2S_3, because the precipitates of the latter class of substances have a small amount of chemical affinity for the coagulating ions.

[1] Thesis for D.Sc. degree. Allahabad University, Allahabad.
[2] J. Phys. Chem., **24**, 30 (1920).
[3] Z. physik. Chem., **83**, 97 (1923).

If by any means we can find out the amount of adsorption of an electrolyte by a definite weight of the sol and its freshly obtained precipitate immediately after its formation, we shall find that the difference between the two values expressed in moles would be greater in the case of univalent ions than in the

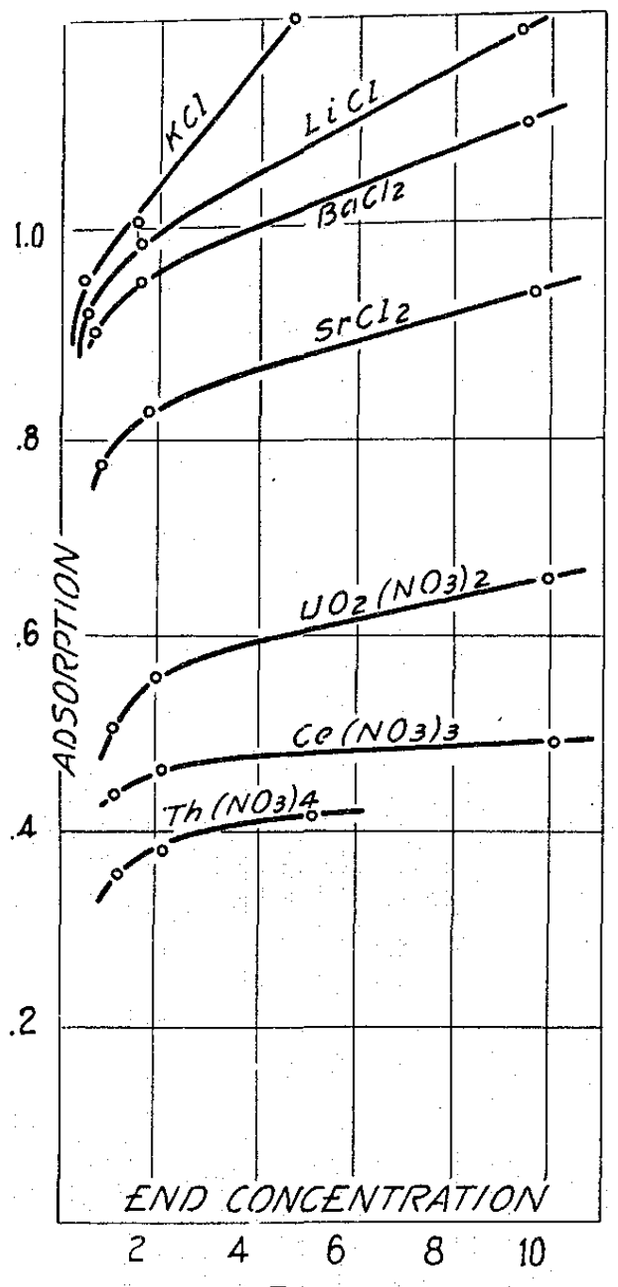


FIG. 3
Adsorption of cations by precipitated MnO_2.

case of polyvalent ions, because this difference arises from the adsorption due only to charge neutralisation of a sol and to this difference only, the Schulze-Hardy law is rigidly applicable.

Experiments with freshly precipitated Hydrated MnO_2

In order to test the above point experimentally, we have carried on experiments on the adsorption of cations by freshly precipitated MnO_2. The method of preparation was that of Sirkar and Dhar[1]. The manganese dioxide

[1] Z. anorg. Chem., **121**, 135 (1922).

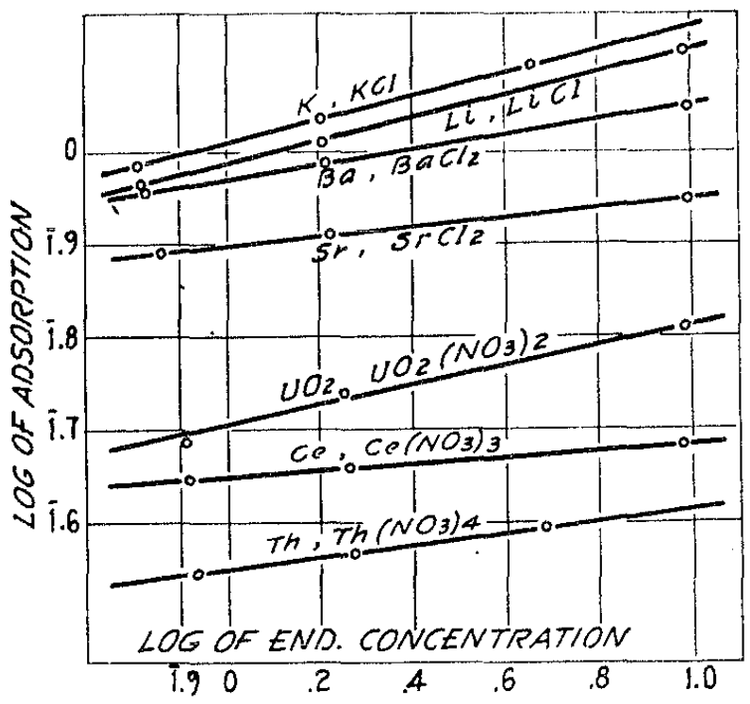


FIG. 4
Adsorption of cations by precipitated manganese dioxide.

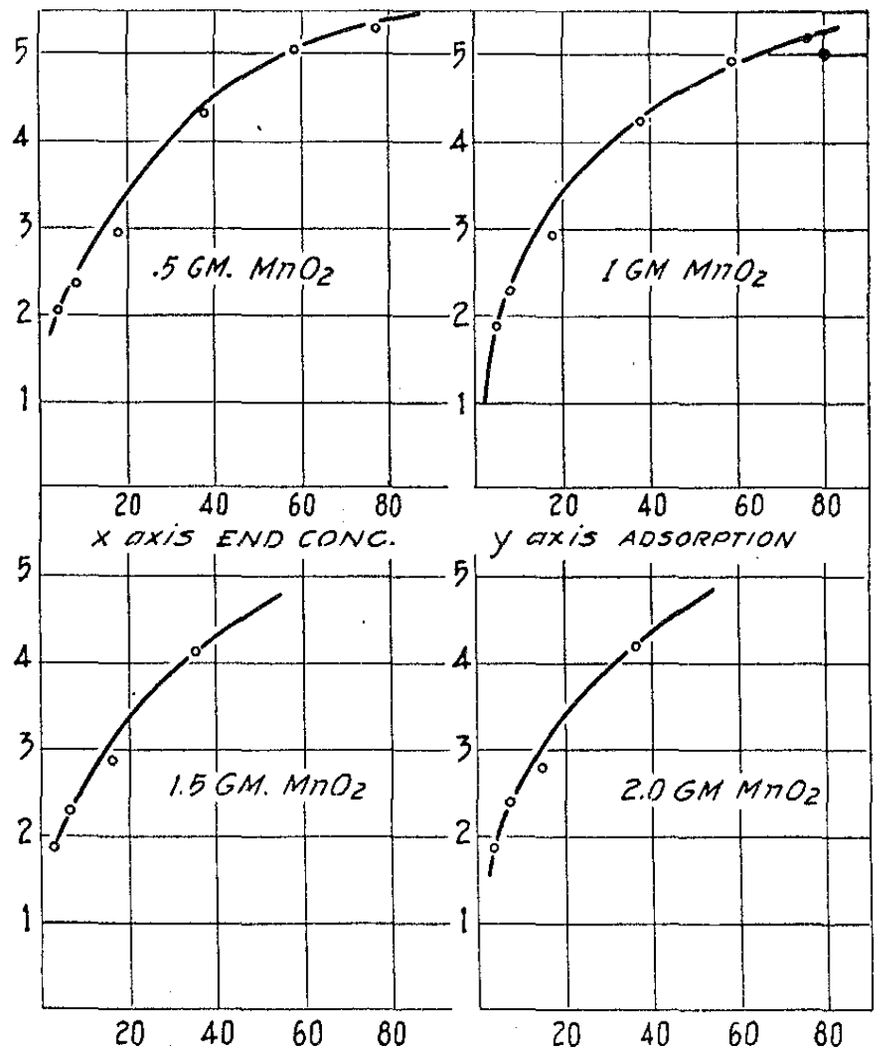


FIG. 5
Adsorption of $AgNO_3$ by precipitated MnO_2.

precipitate was prepared by the interaction of $MnSO_4$ and $KMnO_4$, in presence of a strong solution of an oxidising agent like KNO_3. The reaction was carried on at the ordinary temperature. The precipitate was freed from all traces of electrolytes and then was dried at the ordinary temperature.

The manganese-dioxide was estimated both gravimetrically and volumetrically and the mean result show that the sample contained 74 percent MnO_2, the rest being water, Tables III-V and Figs. 3-6.

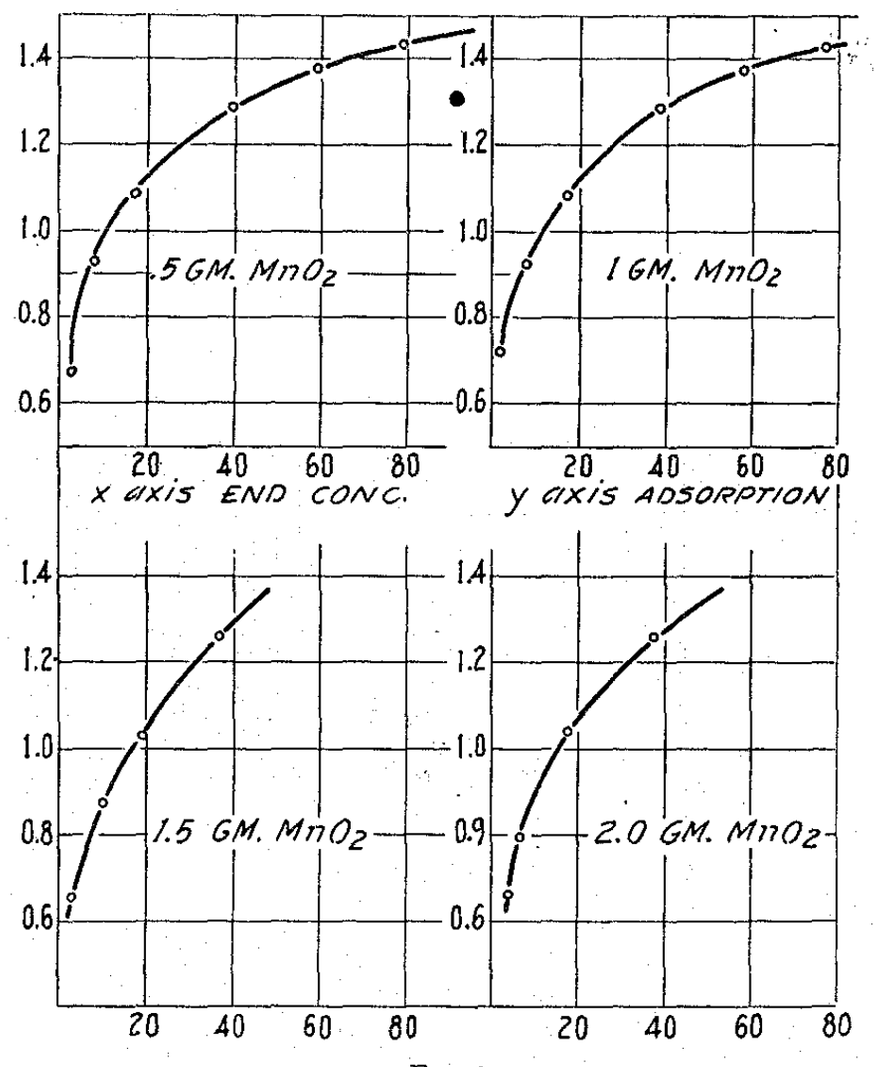


FIG. 6
Adsorption of $CuCl_2$ by MnO_2.

TABLE III

Sample contained 74% MnO_2; volume of solution = 50 cc.; amount of manganese dioxide used = 0.5 gm.; time = 20 hours

Initial concentration in millimoles per 50 cc.	End. conc. in millimoles per 50 cc.	Adsorption per gm. of MnO_2 in millimoles
	$UO_2(NO_3)_2$	
10.00	9.7610	0.646
2.00	1.7960	0.552
1.00	0.8210	0.483
	$Al(NO_3)_3$	
10.00	9.8600	0.430
2.00	1.8800	0.370
	$BaCl_2$	
10.00	9.5900	0.108
2.00	1.6450	0.959
1.00	0.6650	0.905
	$Ce(NO_3)_3$	
10.00	9.8260	0.475
2.00	1.8330	0.454
1.00	0.8350	0.443
	$SrCl_2$	
10.00	9.6730	0.883
2.00	1.6950	0.824
1.00	0.7280	0.762
	LiCl	
10.00	9.5530	1.208
2.00	1.6240	1.016
1.00	0.6600	0.919
	$Th(NO_3)_4$	
5.00	4.8550	0.391
2.00	1.8650	0.365
1.00	0.8700	0.350
	$HgCl_2$	
5.00	4.7250	0.979
2.00	1.7300	0.729
1.00	0.8570	0.385
	KCl	
5.00	4.5390	1.212
2.00	1.6020	1.075
1.00	0.6440	0.962
10.00	9.5380	1.250

TABLE IV

Sample contained 74% MnO_2; volume of solution = 20 cc.; time = 20 hours; substance adsorbed = $AgNO_3$.

Initial concentration in millimoles per 30 cc.	End conc. in millimoles per 20 cc.	Adsorption in millimoles per gm. of MnO_2
0.50 grams of hydrated manganese dioxide used.		
4M— 80.00	78.170	5.202
3M— 60.00	58.130	5.054
2M— 40.00	38.425	4.156
M— 20.00	18.938	2.871
.5M— 10.00	9.150	2.297
.25M— 5.00	4.255	2.013
1.00 grams of hydrated manganese dioxide used.		
4M— 80.00	76.200	5.135
3M— 60.00	56.310	4.986
2M— 40.00	36.892	4.200
M— 20.00	17.905	2.831
.5M— 10.00	8.315	2.277
.25M— 5.00	3.604	1.886
1.50 grams of manganese dioxide used.		
2M— 40.00	35.428	4.119
M— 20.00	16.897	2.794
.5M— 10.00	7.492	2.259
.25M— 5.00	2.925	1.870
2.00 grams of hydrated manganese dioxide used.		
2M— 40.00	33.936	4.097
M— 20.00	15.876	2.792
.5M— 10.00	6.364	2.456
.25M— 5.00	2.300	1 823

TABLE V

Sample contained 74% MnO_2; volume of solution = 50 cc.; time = 20 hours; substance adsorbed = $CuCl_2$

Initial concentration in millimoles per 20 cc.	End conc. in millimoles per 20 cc.	Adsorption in millimoles per gm. MnO_2
0.50 grams of manganese dioxide used.		
4M— 80.00	79.470	1.432
3M— 60.00	59.490	1.378
2M— 40.00	39.520	1.297
M— 20.00	19.600	1.080
.5M— 10.00	9.660	0.919
.25M— 5.00	4.750	0.675

TABLE V (continued)

Initial concentration in millimoles per 20 cc.	End. conc. in millimoles per 20 cc.	Adsorption in millimoles per gm. MnO_2
1.00 grams of manganese dioxide used.		
4M—	80.00	78.960	1.405
3M—	60.00	58.990	1.365
2M—	40.00	39.150	1.284
M—	20.00	19.208	1.070
.5M—	10.00	9.331	0.904
.25M—	5.00	4.468	0.719
1.50 grams of manganese dioxide used.		
2M—	40.00	38.583	1.275
M—	20.00	18.886	1.027
.5M—	10.00	9.017	0.886
.25M—	5.00	4.257	0.667
2.00 grams of manganese dioxide used.		
2M—	40.00	38.153	1.249
M—	20.00	18.464	1.037
.5M—	10.00	8.700	0.878
.25M—	5.00	4.030	0.655

From the above data, it would be clear that, in the range of concentration of the electrolytes varying from M/5 to M/50 the adsorption for one gram of MnO_2, decreased in the following order;—

Ag > K > Li > Cu > Ba > Sr > UO_2 > Ce > Al > Th.

(the data for Ag and Cu have been obtained by extrapolating the graphs at the higher concentrations)

Comparing this order with the order for the sol given on page 1002, we see that the orders are very nearly the same.

If from the graphs we find the difference of the adsorptions by the sol and the precipitated dioxide, both expressed per gram of MnO_2, for the concentrations M/10, M/25, M/50, we get the results in Table VI.

TABLE VI

Electrolytes	Concentration M/10	M/25	M/50
KCl	4.200	4.000	4.110
LiCl	2.400	2.950	2.870
$BaCl_2$	1.110	1.180	1.000
$UO_2(NO_3)_2$	1.440	1.510	1.460
$SrCl_2$	0.800	0.800	0.810
$Ce(NO_3)_3$	0.900	0.992	1.140
$AgNO_3$	——	about 4.0	
$Th(NO_3)_4$	——	about 0.3	
$Al(NO_3)_3$	——	about 0.4	
$CuSO_4$	——	about 2.5	

In the adsorption experiments by precipitated manganese dioxide, the actual amount of the adsorbent was much greater than that corresponding to the amount of the sol used. Hence in order to get exactly comparable results, we have repeated the experiments with exactly the same amount of precipitated manganese dioxide as was used with the experiments with the sol and the results in Table VII are obtained:—

TABLE VII

Electrolyte	Initial Concentration	Adsorption per gm. MnO_2 (millimoles)		
		By the sol	By the ppt	Difference
$UO_2(NO_3)_2$	M/5	2.250	1.041	1.209
$BaCl_2$	M/5	2.400	1.203	1.197
$Ce(NO_3)_3$	M/5	1.650	0.510	1.140
$SrCl_2$	M/5	1.680	0.921	0.759
LiCl	M/5	4.236	1.362	2.874
KCl	M/10	5.622	1.320	4.302
$CuCl_2$	M/5	5.100	0.902	4.198
$CuSO_4$	M/5	5.310	1.120	4.190

The order of the difference in the adsorption of the cations by the sol and the same weight of the precipitated manganese dioxide from Table VI is;—

$$K > Ag > Li > Cu > UO_2 > Ba > Ce > Sr > Al > Th.$$

and the same order from the Table VII is the following;—

$$K > Cu > Li > UO_2 > Ba > Ce > Sr.$$

Therefore here too, we get, that the cations of the higher valency are generally adsorbed to a lesser extent. Now this order represents the order of adsorption due mainly to charge neutralisation, and the greater the valency of the cation the less the adsorption, which supports the Schulze-Hardy law.

It must be emphasised that the adsorption of ions by the precipitated and air-dried sample of manganese dioxide, which we have used in our experiments, must be less than that obtainable with a sample of manganese dioxide immediately after its precipitation, because the air-dried sample becomes aged more than the sample obtained just after its precipitation. Unfortunately it is not possible to realise experimentally with exactitude the adsorption by the sample obtained immediately after its charge neutralisation, because the precipitate has to be washed free from electrolytes and dried, and by this process it becomes partially aged and the adsorptive power becomes less. Consequently the true adsorption due to charge neutralisation is impossible to determine. What we have obtained is merely an order and not the actual adsorptions. If by any means one could obtain the true adsorption due only to charge neutralisation, it will be much less than those we have obtained.

Some years ago Weiser and Middleton determined the adsorption of various acids by sols of $Fe(OH)_3$ and $Al(OH)_3$. The results given in Table VIII were obtained by them.

TABLE VIII

Anion	Adsorption in millimoles per gram of oxide, yielded from hydroxides	
	Fe_2O_3	Al_2O_3
Citrate	.5018	——
Tartrate	.6232	——
Oxalate	.4364	.5710
Sulphate	.3804	.4984

The results of Sen, with a freshly precipitated samples of $Fe(OH)_3$, and $Al(OH)_3$ are given in Table IX;—

TABLE IX

Anion	Adsorption in millimoles per gram of oxide, yielded from hydroxides	
	Fe_2O_3	Al_2O_3
Citric	2.581	2.349
Racemic	1.917	1.904
Oxalic	2.065	1.866
Sulphuric	1.696	1.793

It will be observed from Tables VIII-IX that the adsorption by freshly precipitated ferric and aluminium hydroxides, expressed per gram of the oxides is much greater than the adsorption per gram of the oxides in the case of the sols. This is a very peculiar behaviour, but by observing their modes of preparation of the samples, we find that this can be very easily explained.

It has been repeatedly observed that the adsorptive power and chemical reactivity of a substance become less when the substance is heated; in other words the phenomenon of ageing of the substance is greatly increased when heated. It has been also observed that the catalytic decomposition of hydrogen peroxide by manganese dioxide is much less when the same weight of the oxide is used which has been heated, than when the unheated oxide is used as a catalyst. Weiser and Middleton prepared their sol by hydrolysing $FeCl_3$ in boiling water. Consequently the sol became aged and lost the chemical reactivity as well as the power of adsorption appreciably. We have observed that ferric hydroxide prepared by the coagulation of a sol of the same substance, in the hot condition does not readily dissolve in dilute HCl; but the freshly precipitated hydroxide at the ordinary temperature dissolves readily in dilute acids. Consequently the chemical reactivity and along with it the adsorptive power of the sol in the hot condition is much less than that of the freshly precipitated hydroxide obtained in the cold. Sen, prepared his precipitate at the ordinary temperature and hence it did not age rapidly or lose the power of chemical affinity and adsorption as much as, in the case of the sol prepared by Weiser and Middleton. If the freshly precipitated substance and the sol are both prepared either in cold or in the hot, the results of adsorption will be comparative and it will be found that the adsorption of electrolytes per gram of the sol will be greater than that obtained in the case of the freshly

precipitated substance, because in the case of the sol, as we have already said, some part of the adsorption should go to neutralise the charge on the sol. In our own experiments on manganese dioxide we have prepared the sol and the freshly precipitated oxide both at the ordinary temperature and so the results are comparable, and it has been definitely established that the amount of adsorption in the case of the sol is greater, than that in the case of the precipitated substance, and the difference seems to be nearly the same for substances of the same valency of the cation, as well as, the difference in the case of polyvalent cations is less than that in the case of monovalent cation as is expected from the fact that the polyvalent cations contain more charge than the monovalent ones.

In a paper[1] previously published from this laboratory, it was shown that freshly precipitated manganese dioxide adsorbs bases more than acids, and the results given in Table X were obtained.

TABLE X

Solution used	Amount of H·, or OH′ present originally	Amount of H·, or OH′ adsorbed
H_2SO_4	0.0094 grams of H·	0.0003 grams of H·
CH_3COOH	0.0162 " "	0.00038 " "
NaOH	0.0170 " "	0.0080 " "
"	0.0340 " "	0.0110 " "
KOH	0.0170 " "	0.0080 " "
"	0.0340 " "	0.0110 " "

We have extended these observations with both, freshly precipitated substance, and the sol of manganese dioxide and our results are given in Table XI.

TABLE XI

Solution used	Amount of H· or OH′ present originally	Amount of H· or OH′ adsorbed
KOH	2.50 gram of OH′	1.30 gram of OH′
"	2.00 "	1.25 "
"	1.00 "	0.80 "
NaOH	2.50 "	1.25 "
"	2.00 "	1.20 "
"	1.00 "	0.80 "
HNO_3	5.00 "	0.144 "
"	2.00 "	0.130 "
"	1.00 "	0.103 "
CH_3COOH	5.00 "	0.120 "

[1] Kolloid-Z., **33**, 18 (1923).

From the foregoing results it is definitely proved that the amount of alkali adsorbed by one gram in the precipitated condition is even ten times greater than the amount of the acid adsorbed by the same amount of manganese dioxide.

The above results confirm the following statement from a paper previously published from these laboratories.[1]

"It appears therefore that hydrated MnO_2 which behaves like H_2MnO_3 and is also acid to litmus can adsorb large quantities of OH ions, because an acidic substance has a great affinity for hydroxyl ions."

"The amount of adsorption of acids by silica or manganese dioxide is very small and is only a few percent of the total quantity of acids taken. This adsorption is more or less due to the surface effect, but the adsorption of bases by the two substances is connected with the chemical affinity, and is more permanent."

Recently Mukherji[2], has stated that silica can adsorb acetic, citric, salicylic, hydrochloric acids, etc. This fact has been contradicted several times by Joseph and co-workers[3]. We have observed that hydrated manganese dioxide and its sol can adsorb acetic acid, nitric acid, etc. Similarly we have also observed that silica adsorbs acids to a slight extent. This kind of adsorption is mainly due to surface effects and is insignificant in comparison with the adsorption due to chemical affinity between the adsorbent and the substance to be adsorbed. It has been noticed that the sol of manganese dioxide, which is negatively charged adsorbs fairly large quantities of HCl, which can be explained from the point of view of charge neutralisation, as has been emphasised before.

Discussion of the Results from the Freundlich Formula

Fruendlich adopted the variation of Henry's law[4] which expresses the adsorption of gases by solids, to denote the adsorption process of colloids and precipitated substances, and tested the results experimentally.[5] He obtained the expression

$$\frac{x}{m} = kc^{1/n}$$

where x is the amount adsorbed by m grams of the adsorbent and c the concentration of the solution; k and n are constants.

Various workers[6] have applied this formula to the adsorption by charcoal and other solids, of various electrolytes, non-electrolytes, and dye solutions and the value of 1/n usually lies between 0.11 to 0.50 when the adsorbent is in the powdered form. Freundlich has proved the applicability of the formula for various colloids.

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[1] J. Phys. Chem., **28**, 457 (1924).

[2] Phil. Mag., (6) **44**, 330 (1922).

[3] J. Chem. Soc., **123**, 2022 (1923).

[4] "Kapillarchemie", 147 (1909). See also von Georgievics: Monatsheft für Chemie.

[5] Procter: "Brit. Assn. Rep." **1908**, 201.

[6] Z. physik. Chem., **57**, 385; **59**, 284 (1907); **74**, 689 (1910); J. Chem. Soc., **91**, 1683 (1907).

If the graph be drawn with logarithm of concentration as abscissa and logarithm of adsorption as ordinate, the curve for the given substance ought to be a straight line and the intercept on the axis of Y gives the value of log k and the tangent of the angle of inclination gives 1/n.

The constant k in the adsorption formula is, in ideal case, a natural constant which may be characteristic for the adsorbed substance.

Another fact must be noted that, in the case of pure adsorption, it is conditioned by the decrease of surface tension at the interface between solvent and adsorbent. In 1888, G. Quincke[1] showed that substances which decrease the surface tension must collect about the dispersed phase with the formation of a film.

H. Freundlich has elaborated and experimentally established the theory of adsorption phenomena basing his ideas on Gibbs' Theorem. A substance which diminishes the surface tension on being dissolved will have positive adsorption. Since a marked diminution of surface tension of water by fats, fatty acids, soaps, albumin, and enzymes is characteristic, it is not surprising that these substances are very easily adsorbed. On the other hand it, may be observed quite easily, that an adsorbent like hydrated manganese dioxide can adsorb large quantities of such substances as NaOH, $MgCl_2$, NH_4Cl, $CuSO_4$, etc., though these substances all increase the surface tension of water to a large extent, when they are dissolved. According to Gibbs' equation, in these cases, there ought to be a negative adsorption instead of positive, but this is not the case. It seems therefore that the purely physical conception as introduced by Gibbs is unable to explain the facts even qualitatively.

Biltz[2] found that the distribution of arsenious acid between ferric hydroxide gel and water follows the equation

$$x/m = 0.631\ c^{1/5}$$

If we were to believe that arsenious acid went into solid solution in the gel we should have to conclude, that it has a molecular weight 1/5 as large in the gel as in water. From other observations however, on the contrary, we know that the tendency is for the reverse; so that the assumption, that it dissolves in the gel as a solid solution is untenable.

A substance while swelling adsorbs more water than the solute dissolved, thereby simulating negative adsorption. Herzog and Adler[3] found that talcum powder adsorbed, from sugar solution, more water than sugar. Again the great concentration which the adsorbed substances cause in the dispersed phase, may be associated with changes in its condition, it may be thrown down as a solid. For example if charcoal is shaken with an aniline dye it shows a shimmer of solid dye. Freundlich and Losev[4] showed that the colour bases adsorbed by charcoal from new-fuchsin and crystal violet were changed at the surface of the charcoal and substances with entirely different properties are formed.

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[1] Wied. Ann., **35**, 590 (1888).
[2] Ber., **37**, 719 (1904).
[3] Z. Elektrochemie, **13**, 533 (1907).
[4] Z. physik. Chem., **59**, 284 (1907).

Very peculiar curves have been obtained by Biltz and Steiner[1] for the adsorption of night-blue and victoria-blue by cotton, and Freundlich[2] for the adsorption of strychnine salts by charcoal or arsenious sulphide, as well as G. Dreyer and Sholto[3] for the adsorption of agglutinin by bacteria. In all these cases less substances was taken up by the adsorbent from the concentrated solution than from those of medium concentration.

So far it has been tacitly assumed that there is no affinity between the adsorbent and the dissolved substance. This occurs only in a few exceptional cases. If the adsorption phenomena be guided simply by physical facts then the adsorption ought to be reversible while this is not the case generally. For example Hedin[4] has shown that certain enzymes are irreversibly adsorbed from water. Similar experiments have been done by other workers using wool, filter paper, etc., and from the experiments it is evident that in most cases the chemical nature of the adsorbent plays a very prominent rôle in adsorption phenomena. For example it has been observed that powdered manganese dioxide adsorbs much more of electrolytes than arsenious sulphide or mercuric sulphide which in general adsorbs more than calcium carbonate does. Besides, the facts indicate that the nature of the added substance and the way they are added, play an important part. For example, manganese dioxide adsorbs silver nitrate more than it does copper chloride and so on, and silk adsorbs picric acid more in the aqueous solution than in the case of organic solvents.

It should be mentioned furthermore that supplementary chemical reaction may occur between the adsorbent and the adsorbed substance, which may lead to a fixation, that makes the process irreversible; that is, a true chemical combination may result. The occurrence of this condition is characterised by the fact that it requires a certain lapse of time and in such delayed process, we may say, that a slow diffusion of the adsorbed substance into the adsorbent has taken place. J. Davis[5] has shown it; in the case of charcoal adsorbing iodine.

Thus we see that in the phenomenon of adsorption various complications may arise. The physical view of adsorption has a very limited application, being valid in cases of organic acids, etc., which depress the surface tension of water; on the other hand the chemical view of adsorption which is guided by chemical affinity, has a much wider application.

If we fix our attention on the Freundlich equation

$$x/m = kc^{1/n}$$

we find that $1/n$ is the association factor depending upon the state of molecules in the two phases, while the value of k will be guided by the chemical

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[1] Kolloid-Z., **7**, 113 (1910).
[2] "Kapillarchemie", 147 (1909).
[3] Z. physiol. Chem., **37**, 484 (1903).
[4] Z. physiol. Chem., **50**, 497 (1907); **60**, 364 (1909).
[5] J. Chem. Soc., **91**, 1666 (1907).

affinity of the adsorbent for adsorbed substance. This will be clear if we write down the usual equation for Henry's law:—

$$x/m = kp$$

where k is constant. If the affinity increases it means that for the same concentration of the gas the solid will adsorb more, that is, in that case k will increase. Also the molecular condition of the substance which is being adsorbed will be determined by the substance itself, its surface and its molecular aggregation.

Boswell and Dickson[1] have studied the effect of "ageing" of precipitated ferric hydroxide on its adsorptive power. It was shown that n did not vary much for different preparations of the hydroxide when solutions of arsenious oxide was used; but ageing had a marked effect on k.

Similar experiments of Mecklenburg[2] proved the same thing. In Table XII the results calculated for various preparations are shown.

TABLE XII

Series	Precipitation temperature	1/n	k
Boswell and Dickson			
(1) Pure As_2O_3	—	0.210	128
(2) As_2O_3	Constant NaOH	0.284	333
Mecklenburg	1°	0-183	195
	11°–12°	0.186	184
	23°	0.197	184
	45°	0.186	180
	51°	0.195	170
	60°	0.187	170
	98°	0.195	120

Again Sen has observed in his thesis that when fresh and aged samples of the same preparation are used for difference in the value of k is great while n does not vary much. If, however, different preparations are used n also varies appreciably. Now in the same preparation the probability is that the molecular association will be the same, though with ageing the chemical reactivity may vary greatly and, that is why, we get a large variation of k without corresponding change in the value of n.

From the experimental results of the foregoing authors one fact is noticeable that k decreases appreciably with the ageing of the adsorbent. In other words the chemical affinity of the adsorbent for the substance which is going to be adsorbed decreases appreciably with ageing. Hence the value of k gives us an idea of the chemical affinity of the adsorbent for the substance to be adsorbed.

Freundlich's[3] data for acetic acid, Br_2, and C_6H_5COOH adsorbed by charcoal are given in Table XIII.

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[1] J. Am. Chem. Soc., **40**, 1793 (1918).
[2] Z. physik. Chem., **83**, 609 (1913).
[3] "Kapillarchemie", 147 (1909).

TABLE XIII

Adsorbent	Solution	n	log k
Blood charcoal	CH_3COOH in water	2.35	0.980
"	Br_2 "	2.40	0.970
"	C_6H_5COOH "	2.53	2.320

These show that so long as blood charcoal is used the value of n is approximately constant; but k varies greatly.

Pawlow[1] obtained the results given in Table XIV.

TABLE XIV

Adsorbent	1/n	k
Pressed Coal	0.58	0.050
Unpressed Coal	0.58	0.056

Von E. Ungerer[2] studied the effect of various organic salts on a silicate. His results are given in Table XV.

TABLE XV

Salts	1/n	k
Guanidine hydrochloride	0.734	1.072
Betain "	0.486	0.794
Aniline "	0.246	0.210
Methylamine "	0.927	3.162
Cinchonine "	0.706	0.803
Strychnine "	0.710	1.122
Chinin "	0.660	0.616

From the above data it will be clear that for a given adsorbent the variation of the value of 1/n is not so large as the variation of k, and we actually find that when chemical reactivity is more pronounced we get a higher value of k, while the value of 1/n has hardly any definite relation with chemical reactivity.

Investigation of k and 1/n.—Sen has investigated the adsorption of various acids by hydroxides of iron, aluminium, and chromium and from his results if the values of k or 1/n, are calculated, the following simple relationship will be noticed.

For $Fe(OH)_3$ the value of k for various acids decreased in the following order:—oxalic > malic > racemic > citric > hippuric > succinic > benzoic > propionic > butyric. For $Al(OH)_3$ the order for k is: oxalic > malic > citric > racemic. For $Cr(OH)_3$ the order is: oxalic > malic > citric > racemic > hippuric > succinic > benzoic.

[1] Kolloid-Z., **35**, 221 (1924).
[2] Kolloid-Z., **35**, 228 (1924).

On the other hand, we know that the dissociation constants of the acids are as follows:—

Oxalic	0.100000	Succinic	0.000068
Malic	0.012000	Benzoic	0.000060
Racemic	0.000970	Acetic	0.000018
Citric	0.000820	Butyric	0.000015
Hippuric	0.000220	Propionic	0.000013

If we write the acids in the order of their strengths, we have the following series:—oxalic > malic > racemic > citric > hippuric > succinic > benzoic > acetic > butyric > propionic. Consequently, the order of k for the hydroxides is exactly the same as that of the dissociation constants of the acids which were used in the adsorption experiments.

It must be emphasised that this deduction is based on purely chemical phenomena and the physical effects due to surface tension has not been taken into account. Though there exists some influence due to the latter, yet the former is so very marked that the latter effects may be altogether neglected.

In these experiments the value of 1/n does not vary by more than 10 per-cent and so we are led to a very important generalisation that the value of k and the amount of adsorption are proportional to the dissociation constants of the organic acids, in other words, the chemical affinity of the hydroxides of iron, aluminium, and chromium, is greater, the greater, the dissociation constants of the organic acids.

The view that the constant k depends upon ionisation is further borne out by the experiments of Walker and Appleyard[1] on the adsorption of picric acid by silk in various solvents. It was found that—

TABLE XVI

	k
In aqueous solution	35·5
" alcoholic "	20.5
" benzene "	about 0

and when calcium benzoate was added to the benzene solution it was found that the value of k further decreased. Now the effect of the salt was to drive back ionisation and if the ionisation view is correct we would always expect a diminution of k. Hence the above experiments supports very strongly, the view that other condition remaining the same the greater the dissociation, the greater is the value of k, for we know that in organic solvents there is lesser dissociation and in these experiments also we find that in organic solvents k diminishes.

As has been done in the case of k, we have also calculated 1/n from Sen's results, and the following orders are obtained. For $Fe(OH)_3$:—racemic > malic > benzoic > oxalic > propionic > butyric > succinic > hippuric > citric. For $Al(OH)_3$:—malic > citric > oxalic > racemic. For $Cr(OH)_3$:—

[1] J. Chem. Soc., **69**, 1334 (1896).

racemic > hippuric > citric > benzoic > malic > succinic > oxalic. These orders apparently have no relationship amongst themselves, and this is expected as the power of association of the substance adsorbed depends upon itself and the adsorbent, but at the same time, this point may be noticed that for the three allied hydroxides as Sen has used, the value of 1/n hardly changes beyond 10 percent, when organic acids were used.

From our own results, using precipitated manganese dioxide, and different electrolytes the value of 1/n all lay within ten percent.

Von Wedekind and H. Wilke[1] measured the adsorption of H_2O_2, HCl, $HClO_4$, by a gel of zirconium oxide and the values of 1/n and k are given in Table XVII.

TABLE XVII

Substance	1/n	k
H_2O_2	0.353	13.6
HCl	0.164	42.5
$HClO_4$	0.179	29.9

Here too, in the case of the acids the value of $1/n$ does not change to the same extent as k does, and in the case of HCl a stronger acid, we get k about 50 percent greater than the k obtained in the case of $HClO_4$. The k for H_2O_2 was less than the k for the acids, which might be expected from the fact that H_2O_2 has a lesser affinity for the gel than what the acids have, because zirconium oxide is a basic oxide and has a strong affinity for acids.

The results of Freundlich[2], for charcoal and acetic acid and other organic acids, about all of them gave the values of n as lying between the limits 2 and 2.5.

Hence it becomes clear that the value of n depends upon the adsorbent and the adsorbed substance, and so long as the adsorbent remains the same or of allied properties and the adsorbed substances are similar the value of n does not change rapidly.

It might be of interest to investigate the applicability of the equation of the Freundlich type, over a certain range of concentration. It may be pointed out that Fischer has shown that this equation has a very wide application and may fit in with the results of different experiments which cannot possibly be called adsorption.

From the graphs obtained by us in the cases of $AgNO_3$ and $CuCl_2$, at different concentrations ranging from 4M to 0.25M when the adsorbent was manganese dioxide, one fact will certainly be noticed, that the values of 1/n go on diminishing with increase of concentration.

We shall try to explain the point from simple considerations. As we have already said, the value of k is closely related to the chemical affinity and depends greatly on the degree of dissociation of the electrolyte in question. If the ionisation varies greatly with the dilution, the value of k must necessarily change which can only be possible in a continuous curve by the change

[1] Kolloid-Z., 34, 83, 283; 35, 25 (1924).
[2] "Kapillarchemie", 147 (1909).

in the angle of inclination of the tangent at that point. In this case the tangent represents the value of 1/n, and so, if ionisation changes with the concentration, 1/n must necessarily change. On the other hand if we keep 1/n constant, from our experimental results, we find that the value of k actually decreases with increase of concentration of the electrolytes which supports our view that the greater the dissociation, the greater is the value of k, since with increase of concentration, the degree of dissociation of the electrolyte decreases and along with it the value of k also decreases.

From the experimental results on adsorption by cocoanut charcoal, obtained with gases like CO_2, CH_4, etc., it will be observed that the value of k decreases with increase in the concentration of the gas.

Our results on the adsorption of electrolytes by manganese dioxide, show that if 1/n be kept constant the value of k decreases with increase of concentration.

Another interesting fact to be recorded is, that the lower the temperature at which the adsorption experiments are carried on, the greater is the value of k, in the case of the adsorption of gases like CH_4, this is because at lower temperature the amount of adsorption is much greater than that at a higher temperature and so k which is roughly a measure of chemical affinity, as well as the power of adsorption, also increases.

From our experimental results, it will be seen that the percentage adsorption of electrolytes is greater for a dilute solution than that for the concentrated one though the total amount of adsorption is greater in the latter case, and that is why the value of k becomes greater in the dilute solution than in the concentrated ones.

Now in the case of $AgNO_3$, for example, we have three things in solution, $Ag^{\cdot}$, NO_3', and $AgNO_3$ molecules. For a particular concentration there will be a definite ratio of ions to molecules, depending upon the degree of dissociation of the electrolytes in solution.

If we consider that both $AgNO_3$, and $Ag^{\cdot}$ are adsorbed independently, when hydrated manganese dioxide is put in solution, then the reactions of the following types takes place;—

for ionic:—

$$H_2MnO_3 + 2.\,AgNO_3 = Ag_2MnO_3 + 2\,HNO_3. \qquad (1)$$

for molecular:—

$$H_2MnO_3 + n.\,AgNO_3 \text{ —} (AgNO_3)n.\,H_2MnO_3. \qquad (2)$$

for the acid:—

$$H_2MnO_3 + m.\,HNO_3 = (HNO_3)m.\,H_2MnO_3. \qquad (3)$$

These are all the possibilities. Similar possibilities may be written down for other electrolytes also. In order to find the extent of each of these reaction, we have carried on some subsidiary experiments. We have determined the amount of the liberated acid, obtained in these cases and also we have determined the adsorption of acids by hydrated manganese dioxide.

If a be the amount of the cations adsorbed according to the equation (1) and b the amount of undissociated molecules adsorbed according to the equation (2) and c the amount of acid adsorbed, then the total diminution

of the cations in solution will be represented by a+b, and the amount of acid in solution will be represented by a−c. Since the adsorption of the acid (compare p. 900) is very small, more so, when the concentration of the acid is small, we may neglect the effect c in comparison with b or a.

If x be the concentration of the total cations in solution and $\bar{m}$ the degree of dissociation, then the concentration of the undissociated molecules is,

$$(1-m)X \qquad (4)$$

and for the adsorption of undissociated molecules, we get the equation of the following type,

$$b = K(1-\bar{m})X^{1/n} \qquad (5)$$

where n and K are the usual constants.

Similarly, for the adsorption of ions the equation will be,

$$a = K'\bar{m}X^{1/n'} \qquad (6)$$

where n′ and K′ represent the usual n, K and a the amount of the cations adsorbed according to the equation (1). Then the total adsorption of cations we have

$$x/m = K(1-\bar{m})X^{1/n} + K'\bar{m}X^{1/n'} \qquad (7)$$

If instead of distinguishing between the two equations (5); and (6) and the additive one (7) we were to write the usual Freundlich equation

$$x/m = KX^{1/n'} \qquad (8)$$

we will find that the values of n and K will go on changing with X.

TABLE XVIII

Initial Conc.	Degree of dissociation	Ads. of Ag, (a+b) per gram of MnO_2	HNO_3 liberated a	Amount of $AgNO_3$ ads. b
	0.5 grams of manganese dioxide used (74%)			
2N	0.57	4.257	2.036	2.220
N	0.62	2.870	1.800	1.070
.5N	0.68	2.297	1.528	0.769
.25N	0.75	2.013	1.484	0.529
	1.0 gram of manganese dioxide used (74%)			
2N	0.57	4.200	1.936	2.264
N	0.62	2.831	1.728	1.103
.5N	0.68	2.277	1.257	1.026
.25N	0.75	1.886	1.180	0.706
	1.5 grams of manganese dioxide used (74%)			
2N	0.57	4.119	1.332	2.787
N	0.62	2.792	1.012	1.780
.5N	0.68	2.456	1.000	1.456
.25N	0.75	1.823	0.732	1.091
	2.0 grams of manganese dioxide used (74%)			
2N	0.57	4.097	1.200	2.897
N	0.62	2.792	1.012	1.780
.5N	0.68	2.456	1.000	1.456
.25N	0.75	1.823	0.732	1.091

To test the correctness of this assumption, we have determined the extent of adsorption according to reaction (1); and (2) in cases of adsorption of $AgNO_3$, $BaCl_2$, and $CuCl_2$, and the results are given in Tables XVIII-XX.

TABLE XIX

Initial conc.	Degree of dissociation	Ads. of Cu, (a−b) per gram of MnO_2	(HCl_2) liberated a	Amount of $CuCl_2$, ads. b
	0.5 gram of manganese dioxide used (74%)			
2M	0.20	1.297	0.480	0.817
M	0.32	1.080	0.320	0.760
.5M	0.51	0.919	0.200	0.719
.25M	0.61	0.675	0.160	0.515
	1.0 gram of manganese dioxide used (74%)			
2M	0.20	1.284	0.391	0.893
M	0.32	1.070	0.328	0.750
.5M	0.51	0.904	0.230	0.674
.25M	0.61	0.719	0.180	0.539

TABLE XX

Initial conc.	Degree of dissociation	Ads. of Ba, (a−b) per gram of MnO_2	(HCl_2) liberated a	Amount of $BaCl_2$, ads. b
	0.5 gram of manganese dioxide used (74%)			
0.10M	0.759	1.108	0.900	0.208
0.04M	0.834	0.959	0.846	0.113
0.02M	0.850	0.905	0.801	0.104

In all these experiments, if the logarithms of the concentration of the ions or the molecules at a certain concentration be plotted as abscissa and the logarithm of the amount of adsorption per gram of MnO_2, of ions and molecules be plotted as ordinates, we actually get approximately straight lines, which prove that the Freundlich equation may be applicable with the limitation that we ought to consider the summational equation (7) in place of only one equation of the form shown in (8).

Since $\bar{m}$ is a complicated function of X it will be better to consider the equations graphically.

Having proved the plausibility of the assumption let us investigate how the values of 1/n ought to vary with concentration.

If we draw the curves for $\bar{m}-x$, and if we imagine for simplicity $k^- = k' = 1$ and n = say 2, and $n' = 3$ and if we draw the corresponding curves for ionic and molecular adsorptions we can obtain the summational curve of the type (7). By actually drawing such a curve for silver nitrate it will be found that 1/n varies from 0.46 to about 0.40, between the limits of concentration 0.25N to 2N. Thus we see that the variation of 1/n actually happens, and as it tallies with the experimental decrease of 1/n, it is very probable that the

adsorption of ions and molecules take place independently of one another and depends upon their respective concentrations in solution. Similar results are obtainable for $BaCl_2$ and $CuCl_2$, showing that ionic and molecular adsorptions takes place when hydrated manganese dioxide is shaken with solutions of these electrolytes.

From the results given on pp. 1021 and 1022 it will be observed that the amount of acid set free are not equivalent but are much less than the amount of adsorption of the cation. Consequently the equations usually applied in explaining the chemical changes of adsorption phenomena are not at all quantitative.

(1) $2AgNO_3 + H_2MnO_3 = Ag_2MnO_3 + 2HNO_3$
(2) $2CuCl_2 + H_2MnO_3 = CuMnO_3 + 2HCl$
(3) $2BaCl_2 + H_2MnO_3 = BaMnO_3 + 2HCl$

In our experiments on the adsorption of acids like HNO_3, CH_3COOH, we have found that even less than 3% of the acid is adsorbed; hence the amount of decrease in the quantity of acids set free according to the above equations can only be explained to the extent of at most 3%. The amount of the acid set free in the solution when manganese dioxide is shaken with electrolytes is even less than half the amount, which ought to be set free according to the above equations. Hence we have to discard the idea that the acid is adsorbed and must take recourse in the view of molecular adsorption as we have done.

Another interesting fact will also be observed that, as the concentration of $AgNO_3$ or $CuCl_2$ is decreased, the amount of the acid set free do not decrease to the same extent. This again is consistent with our assumption, as in the concentrated solution more of the undissociated molecules are present and so relatively more adsorption of undissociated molecules is possible and hence smaller amount of HNO_3 or HCl is set free. On the other hand in dilute solutions there are very few undissociated molecules and hence the ionic adsorption is greater, which again gives out relatively more acid.

Influence of the change of the volume of the solution and the mass of the adsorbent on the amount of adsorption:—We have so far considered the adsorption of various solutes by manganese dioxide, and it may be noticed that in all cases we have kept the volume of the solution constant. So even if there be any influence of the volume on the amount of adsorption, this has not crept into our observations.

Many experiments have been done to investigate into the influence of the volume of the solution when the concentration remains the same regarding the amount of adsorption, but no explanation has been given for the peculiar behaviours.

TABLE XXI

Initial concentration	Adsorption per gram of MnO_2		
	Vol–20 cc.	Vol–30 cc.	Vol–40 cc.
0.605 N	0.1548 g	0.1710 g	0.1842 g
0.302 N	0.1267 g		0.1412 g

Chatterji and Dhar[1], obtained the results for manganese dioxide and silver nitrate given in Table XXI.

Pawlow[2], obtained the results given in Table XXII for the same pair of substances.

TABLE XXII

Initial concentration (millimoles per litre)	Adsorption per gram of MnO_2 (millimoles per litre)	
	Vol–100 cc.	Vol–300 cc.
22.6180	0.5083	0.6150
40.1864	0.5868	0.7238
90.3320	0.6886	0.7640
188.8290	0.8404	1.0705
456.7633	0.9416	1.1468

Sen has obtained for freshly precipitated ferric hydroxide the results given in Tables XXIII-XXV.

TABLE XXIII

Initial concentration of As_2O_3 in grams per 100 cc.	Adsorption of As_2O_3 in grams per	gm. of $Fe(OH)_3$
	Vol–100 cc.	Vol–50 cc.
0.1928	0.05943	0.05604

TABLE XXIV

Initial concentration of H_2SO_4, milliequivalents per litre	Adsorption of H_2SO_4 milliequivalents per gm. $Fe(OH)_3$	
	Vol–100 cc.	Vol–50 cc.
0.491	0.3792	0.2456

TABLE XXV

Initial concentration of C_6H_5COOH, milliequivalents per litre	Adsorption of C_6H_5COOH milliequivalents per gm. $Fe(OH)_3$	
	Vol–100 cc.	Vol–50 cc.
7·358	0.3301	0.2736

Sen has also obtained the results given in Table XXVI with As_2O_3 when the adsorbents were $Cr(OH)_3$, and $Al(OH)_3$ respectively;—

TABLE XXVI

Adsorbent	Adsorption of As_2O_3 in gm.				
	Vol = 60 cc	70 cc	80 cc	90 cc	100 cc
	Concentration of As_2O_3 is 0.1971 grams per 100 cc.				
$Al(OH)_3$	.0388	.0396	.0406	.0413	.0419
	Concentration of As_2O_3 is 0.2278 grams per 100 cc.				
$Cr(OH)_3$	.1319	.1501	.1650	.1808	.1955

Von E. Wedekind and Wilke[3], obtained the following result with a sample of zirconium oxide using H_2O_2, HCl, and $HClO_4$, as the adsorbed substances;—

[1] Kolloid-Z., **33**, 18 (1923).
[2] Kolloid-Z., **35**, 375 (1924).
[3] Kolloid-Z., **35**, 25 (1924).

TABLE XXVII

Adsorbed substance		Adsorption of H_2O_2, HCl, $HClO_4$ respectively expressed in ccs. by 3 gms. of the gel						
	Vol	20 cc.	30 cc.	40 cc.	50 cc.	80 cc.	125 cc.	
H_2O_2		18.0	24.6	35.1	47.1	58.9	———	
HCl	Vol	42 cc.	50 cc.	60 cc.	90 cc.	150 cc.	300 cc.	
		40.6	46.8	53.2	66.3	83.3	107.5	
$HClO_4$	Vol	30 cc.	40 cc.	50 cc.	70 cc.	100 cc.	150 cc.	150 cc.
		29.1	37.1	42.8	50.5	58.4	66.2	67.0

In all these cases it will be observed that when the concentration remains the same the amount of adsorption increases with the increase of volume of the solution.

The influence of mass is not so important as will be clear from our tables for silver nitrate, copper chloride, given on pp. 1008 and 1009. In all these experiments the effect noticed was hardly greater than the experimental error. So we cannot say anything about it with definiteness. Recently Sen[1] has observed that the effect of the mass of the adsorbent on the amount of adsorption is quite definite, but if we were to examine his data critically we would find that in the tables the maximum percentage difference between his calculated and the experimentally obtained values is even 8.0% while if we were to calculate all the results with the same values of k and n in the usual expression, i.e. neglecting the effect of mass altogether, we would find that the percentage difference of the calculated and the observed values can be made to vary within 5 to 6 percent. On the strength of his observations therefore it is difficult to speak of any effect of mass of the adsorbent. Or in other words, we are of the opinion that experimental results show that there is no effect of the varying amounts of the adsorbent on the adsorption, expressed per unit mass of the adsorbent. This point will be considered again hereafter.

Pawlow has done a lot of work on adsorption of different substances by charcoal, manganese dioxide, hide powder, etc., etc. His results may be summarised as below:—

Silver nitrate by manganese dioxide[2]. He has obtained that the greater the volume of the solution, of a definite concentration, the greater is the amount of adsorption. He has also obtained some results to show that the amount of adsorption per gram of the adsorbent is slightly greater when the amount of the adsorbent is greater, especially at low concentrations. This seems to be due to experimental error, as our experimental results show that by increasing the amount of the adsorbent, only a very slight decrease is obtained, when the adsorption is expressed per unit mass. Again at higher concentration of

[1] Unpublished work.
[2] Kolloid-Z., **35**, 375 (1924).

the electrolytes he gets the results exactly similar to our own and consequently we are of the opinion, that the results obtained by Pawlow with dilute solutions of the electrolytes, are not accurate.

Blood charcoal and acetic acid[1]. Some peculiar results have been obtained by Pawlow, when the concentration of the acid is small; by using larger volume of acetic acid, of the same concentration, greater adsorption is observed, which is in agreement with our results on manganese dioxide. If, however the concentration of the acid is greater the amount of adsorption, becomes less with larger volume. This result is difficult to explain, and it seems that they are due to experimental error. Consequently we are of the opinion that the change of volume has no effect on adsorption. These results of Pawlow indicate that this adsorption is more of a physical phenomenon.

Hide powder by chrome alum[2]. Here too Pawlow gets peculiar results. When the mass of the adsorbent remains the same and the volume is increased the concentration being maintained the same, the amount of adsorption is greater when lesser volume is used. This is maintained at all concentrations; while if the volume be maintained constant the amount of adsorption per unit adsorbent becomes less when lesser mass is used. The same is the case for pressed powder; it is impossible to correlate these facts, as they contradict other experiments of the same nature.

Soil and ammonium chloride[3]. When the mass of the soil is the same, the amount of the salt is the same, the adsorption increases with the increase of the total volume, which is quite contradictory, as by increasing the volume, the concentration is diminished; and the effect of concentration is much greater than the effect of volume and so it is surprising how he could obtain such results. In all the literature on this subject it is hard to find any other case of the like nature. When the mass of the soil remains the same the concentration of the electrolyte the same the adsorption markedly increases with the increase of the volume. When the total solute and the total volume are the same the amount of adsorption per unit mass decreases with increase of mass.

From these results it appears that the influence of mass is very slight. No doubt it will be observed, that if we take it into account at all, it slightly diminishes with increase of mass. The effect of volume is quite definite—that it increases with increase of volume.—Consequently it appears that the amount of adsorption not only depends upon the concentration of the electrolyte, but also upon the total amount of the electrolyte available for assorption, and these peculiar results are very difficult to explain.

From what has been said above, it will be clear that when we are considering the adsorption by charcoal, soil, etc., there is hardly any effect due to chemical affinity of the adsorbent for the substance to be adsorbed. The equation of the Freundlich type is generally applicable to these cases, but

[1] Kolloid-Z., **35**, 225 (1924).
[2] Kolloid-Z., **35**, 21 (1924).
[3] loc. cit.

when we are considering substances like MnO_2, or the hydroxides of iron, chromium, and aluminium, we are dealing with a surface which is chemically active and the usual physical processes cannot be applied to these cases. It might be seen that when the concentration of the electrolytes are small we get the law obeyed, yet in the sphere of higher concentration marked deviation occurs. Even if we find in a certain process that the Freundlich equation is obeyed, we cannot jump to the conclusion that it is an adsorption phenomenon, for Fischer has shown that the law might be found to govern quite different phenomena. In the light of this idea, the purely adsorption curves cannot be taken as proof of the nature of the process. Mecklenburg[1], studied the adsorption of phosphoric acid by stannic oxide and concluded that it is a case of adsorption. Wedekind and Wilke[2], studied the adsorption of phosphoric acid by a gel of zirconium oxide. Wagner[3], has shown that salts of aluminium, iron, etc., when hydrolysed can adsorb the free acid to a certain extent. The adsorption of bases by acidic substances has long been known for König[4], in 1882 noticed that humus will take up ammonia from ammonium sulphate solution. Odén[5], has recently proved that humus is acidic and it forms soluble salts with ammonia. Although in some of these cases the adsorption formula of Freundlich is applicable, yet the chemical affinity of the basic substance, like ferric hydroxide mainly controls the adsorption of acidic substance. In the adsorption of phosphates by soils and in the study of soil acidity, this theory has been practically applied by Cameron[6], Harris[7], and others[8]. Chatterji and Dhar[9], studied the adsorption of the same type as we have done; and the results of Ganguly and Dhar[10], all point to the chemical nature of the adsorption process taking place with manganese dioxide. In a recent paper, W. Cholpin and A. Balandin[11], have shown that the adsorption of $BaCl_2$ by manganese dioxide is of a chemical nature. It is well known that many manganites are supposed to exist and this fact also supports the possibility of a chemical reaction between a base and manganese dioxide. It is obvious from these results that our view—that the chemical affinity plays a great part in the adsorption phenomena—receives considerable support. It is very difficult to say, whether definite chemical compounds are formed by the interaction of MnO_2, hydrated, and different electrolytes.

Silver manganites. Chatterji and Dhar's[12] results point to the following adsorption compounds:—$2Ag_2O.3MnO_2.xH_2O$, $Ag_2O.3MnO_2.xH_2O$, $7Ag_2O.6MnO_2.xH_2O$, $Ag_2O.12MnO_2.xH_2O$, $Ag_2O.23MnO_2.xH_2O$, etc., etc.

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[1] Z. anorg. Chem., **74**, 215 (1912).
[2] Kolloid-Z., **34**, 83 (1924).
[3] Monatsheft, **34**, 95 (1913).
[4] Landw. Jahrb., **11**, 1 (1882).
[5] Trans. Faraday Soc., **17**, 188 (1922).
[6] J. Phys. Chem., **14**, 320, 393 (1910).
[7] J. Phys. Chem., **18**, 355 (1914).
[8] J. Landw., **60**, 111, 197 (1912); J. Agric. Sci., **8**, 65 (1916).
[9] loc. cit.
[10] loc. cit.
[11] Z. anorg. Chem., **149**, 157 (1925).
[12] loc. cit.

Ganguly and Dhar's results give:—$Ag_2O.4MnO_2.xH_2O$.

Our results point to the following: $Ag_2O.4MnO_2.xH_2O$, $Ag_2O.2MnO_2.xH_2O$, $Ag_2O.MnO_2.xH_2O$, $3Ag_2O.2MnO_2.xH_2O$, etc., etc.

Copper manganites—Chatterji and Dhar's results give the following adsorption compounds: $CuO.4MnO_2.xH_2O$, $CuO.17MnO_2.xH_2O$, $CuO.9MnO_2.xH_2O$, $2CuO.15MnO_2.xH_2O$, $CuO.6MnO_2.xH_2O$, etc., etc.

Ganguly and Dhar's results give: $CuO.7MnO_2.xH_2O$, etc., etc.

Our results point to the following compounds: $CuO.2MnO_2.xH_2O$, $CuO.5MnO_2.xH_2O$, $CuO.8MnO_2.xH_2O$, etc., etc.

Similarly the existence of many more compounds may be formulated. There is hardly any probability of so many definite chemical compounds. So we conclude that these are intermediate between true chemical compounds on the one hand, and the mixtures obtained by purely physical adsorption on the other like ammonia on charcoal, hydrogen on palladium etc.

Investigation of a positively charged Sol of Manganese Dioxide

In previous papers published from these laboratories, it has been proved that a positively charged sol like ferric, aluminium, and chromium hydroxides adsorbs ions carrying the same charge as the sol only to a slight extent. On the other hand, the negatively charged sol like arsenious sulphide, antimony sulphide, etc., appreciably adsorbs ions carrying the same charge as the sol. It has been proved that a negatively charged sol adsorbs mainly the positive portions of the salt solution and adsorb the negative portion only slightly.

We have prepared a positively charged manganese dioxide sol, and we find that it adsorbs ions carrying the same charge as the sol to an appreciable extent. When the manganese dioxide sol is prepared by the method already indicated, we get a sol negatively charged, but the positively charged sol is prepared in the following way. A normal solution of ferric chloride is prepared and this is mixed with a standard solution of $KMnO_4$. Hydrogen peroxide is then added to this mixture in small quantities at a time and the mixture stirred well. When there is hardly any excess of permanganate, the reaction is stopped and this is then dialysed for about ten days till the dialysed liquid is free from iron, chloride and KOH.

It will be seen that when cupric chloride is added to the positively charged sol it will attract and adsorb the positive ions because of its chemical affinity for copper. It may also be seen to adsorb the negative ions and molecular salt. Now when the charge in the sol is neutralised by the adsorption of negative ions the neutralised particles may easily adsorb cupric ions because of its chemical affinity. It is quite probable that when the charge on the sol becomes sufficiently small, it might attract copper ions due to chemical affinity, which might even counterbalance the repulsive force due to the sameness of electric charge.

The adsorption of positive ions will certainly stabilise positively charged sol and the stability of the sol with respect to its coagulation by a certain electrolyte will depend upon the ratio of the amount of adsorption of the two ions of the electrolyte. For example, when copper chloride is added to the sol,

it will adsorb both copper and chloride ions as has been shown experimentally, although the adsorption of chloride ions is more than that of the copper ions. Hence the sol is actually coagulated by the electrolyte.

TABLE XXVIII

Strength of the sol of positively charged manganese dioxide = 0.320 grams MnO_2 per lit.; volume of sol used = 20 cc.; total volume of the solution = 50 cc.; time = 20 hours.

Initial concentration of ions. (millimoles per litre.)		End. conc. millimoles per litre	Total adsorption millimoles per litre	Ads. (millimoles per gm. MnO_2
		$K_2C_2O_4$		
$K^{\cdot}$	5.00×2			
C_2O_4	5.00	4.9697	0.0303	4.545
	5.00	4.9691	0.3090	4.637
			Mean	4.591
		Na_2HPO_4		
2.$Na^{\cdot}$	5.00×2	9.9817	0.0183	2.745
	5.00×2	9.9819	0.0181	2.715
			Mean	2.730
PO_4'''	5.00	4.9787	0.0213	3.195
	5.00	4.9792	0.0208	3.120
			Mean	3.157
		Ratio PO_4/Na = 1.16.		
		K_2SO_4		
2.$K^{\cdot}$	5.00×2	9.9827	0.0173	2.595
SO_4	5.00	4.9722	0.0278	4.170
	5.00	4.9731	0.0269	4.035
			Mean	4.103
		Ratio SO_4/K = 1.52.		
		$CuCl_2$		
$Cu^{\cdot\cdot}$	5.00	4.9958	0.0042	0.640
2.Cl'	5.00×2	9.9544	0.0456	6.840
		Ratio Cl/Cu = 10.7.		
		$CuSO_4$		
$Cu^{\cdot\cdot}$	5.00	4.9865	0.0135	2.025
SO_4''	5.00	4.9681	0.0316	4.785
		Ratio SO_4/Cu = 2.35.		

In the case of the salts like copper chloride, silver nitrate, etc., with positively charged sol, the ratio of the adsorption of the negative ions to the positive, is usually greater than unity as is shown experimentally. It seems probable that when the concentration of the sol becomes small, this ratio tends to decrease and may approach unity, that is why, more and more of the electrolyte is necessary to coagulate a dilute, positively charged sol of manganese dioxide than one of greater concentration.

From our results, it will be shown that the ratio of the adsorption of the negative ion to the positive decreases with dilution of the sol. This result is analogous to that obtained in the coagulation of a sol of arsenious sulphide by lithium chloride, potassium chloride, etc.

In cases of positively charged sols of the hydroxides of iron, aluminium, and chromium, the adsorption of the positive ions is very small in comparison with the negative ion. The ratio of the amounts of adsorption, of the negative ion to the positive, is always greater than unity and does not much change with the concentration of the sol. For this reason, the general rule—that the greater the concentration of the sol the greater the amount of the electrolyte necessary for coagulation,—is applicable in all dilution of the sols.

The experiments on adsorption were carried on with electrolytes like copper chloride, barium chloride, etc., in order to find out, the amount of adsorption of both the ions of the electrolytes, by a positively charged sol; 20 cc of the sol were put in a clean, dried glass-stoppered bottle and the requisite quantity of water was added to it. A volume of the electrolyte was then put in, the volumes being so arranged, that the total volume was always 50 cc. The bottle was stirred well, and left in the dark for about 20 hours,

TABLE XXIX

Volume of sol used = 10 cc.; other conditions same as in Table XXVIII.

Initial concentration of ions. (millimoles per litre)		End conc. millimoles per litre	Total adsorption millimoles per litre	Ads. (millimoles per gm. MnOt)
		$CuCl_2$		
$Cu^{\cdot\cdot}$	5.00	4.9975	0.0025	0.740
	5.00	4.9976	0.0025	0.740
				Mean 0.740
$2.Cl'$	5.00×2	9.9793	0.0207	6.210
	5.00×2	9.9750	0.0250	7.500
				Mean 6.855
		Ratio Cl/Cu = 9.10.		
		$CuSO_4$		
$Cu^{\cdot\cdot}$	5.00	4.9926	0.0074	2.220
SO_4''	5.00	4.9876	0.0124	3.720
		Ratio SO_4/Cu = 1.70.		

after that time the supernatant liquid was examined and the strength determined with respect to the ions. From the initial concentration, the amount of adsorption was determined by difference, Tables XXVIII-XXIX.

It has been already emphasised that in the adsorption of electrolytes like $CuCl_2$, $CuSO_4$, etc., by positively charged manganese dioxide sol, the ratio of the adsorption of the negative ion to that of the positive, is greater than unity, and that this ratio tends to decrease and it approaches unity as the concentration of the sol is decreased.

By diluting the sol to half the original concentration, the ratio of the adsorption of the negative ion to that of the positive decreased actually. For copper chloride it decreased from 10.70 to 9.10; and for copper sulphate it decreased from 2.35 to 1.70.

The above results conclusively proves that the ratio of the adsorption of the negative ion to the positive decreased with the decrease of the concentration of the sol which supports our explanation of the abnormal behaviour of sols on dilution, towards their coagulation by ions.

Summary

From our experiments on the adsorption of different cations by a sol of negatively charged manganese dioxide during its course of coagulation, the following order has been obtained.

$$Ag > K > Cu > Li > Ba > UO_2 > Sr > Ce > Al > Th$$

This result is similar to the observations of other workers on the adsorption of ions by different sols and show that the higher the valency of the ion the less is the adsorption.

2. The conclusion that the greater the valency of an ion the less is the amount of its adsorption by different adsorbents has been proved to be both experimentally and theoretically satisfactory.

3. The high adsorption observed in many cases for sols of MnO_2, $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$, etc., is mainly due to the adsorption of electrolytes by the freshly coagulated mass than due to charge neutralisation. It has been shown that the interpretation of the Schulze-Hardy law that the greater the valency the less is the adsorption—should be strictly applicable only to those cases where adsorption is primarily due to charge neutralisation.

4. From our experiments on the adsorption of cations both by a sol and a freshly precipitated MnO_2 the difference between the amounts of adsorption for various cations give the following order.

$$K > Ag > Li > Cu > UO_2 > Ba > Ce > Sr > Al > Th$$

This difference arises from the adsorption due mainly to charge neutralisation of MnO_2 sol and the order of adsorption shows that the greater the valency of the cation the less is the adsorption. This supports the Schulze-Hardy law.

5. The results of Weiser and Middleton on the adsorption of ions with sols of $Fe(OH)_3$ and $Al(OH)_3$ show that the adsorption of various ions ex-

pressed per gram of adsorbent is always smaller than that obtained by Sen with freshly precipitated substances; which ought to have been otherwise. This very peculiar behaviour has been explained from the view that Weiser and Middleton used the sol prepared in the hot condition whilst Sen obtained his adsorbents by precipitating them in the cold. Consequently $Fe(OH)_3$ and $Al(OH)_3$ sols lost much of their chemical reactivity and therefore the power of adsorption greatly diminished.

6. It has been shown that MnO_2 is a far better adsorbent of OH ions than H ion this is because MnO_2 is an acidic substance and therefore mainly adsorbs cations.

7. The conclusions from the adsorption formula show that if adsorption be a case of purely physical phenomena $AgNO_3$, $CuCl_2$, etc., ought to diminish the surface tension of water while the reverse is the case.

8. Various complications may arise in the phenomenon of adsorption.

9. An interpretation is given of n and k in the usual Freundlich expression; k has been shown to be dependent upon the strength of acids.

10. The value of n does not change greatly so long as the adsorbent remains the same or of allied properties and the substances adsorbed remain similar.

11. The value of n in electrolytes does not remain constant when the concentration is varied within wide limits but it goes on increasing which can be explained on the supposition that in the solution as the molecules are dissociated the adsorption of ions and molecules take place independently depending upon their individual concentrations in the solution.

12. That the assumption is true is shown by the fact that if the adsorption isotherms be drawn, with respect to the undissociated molecules and the ions, we get the logarithmic curves, approximately straight lines.

13. This same assumption also proves the fact that in the case of adsorption of silver, copper and barium from their solutions we do not get the equivalent quantities of acids set free.

14. It also proves that, relative to the cations adsorbed, the amount of acid set free from a dilute solution is greater than in the case of concentrated solutions.

15. The influence of the change of volume and change of mass has been investigated. For the same concentration the greater the volume of the solution, the greater is the amount of adsorption expressed per unit mass, and the influence of change in the amount of adsorbent has practically no influence on the amount of adsorption expressed per unit mass.

16. This whole investigation supports that the chemical affinity is the preponderating factor in the adsorption phenomena.

17. It is difficult to call the adsorption union as definite chemical compound and so before further light is thrown upon the subject it is better to call them intermediate compounds.

18. The investigation of a positively charged sol of MnO_2 shows that the preponderating factor in the adsorption phenomena is the chemical affinity of the coagulated mass.

19. It has been found that in this case the ratio of negative ion to the positive ion adsorbed is always greater than unity and decreases with the decrease of concentration of the sol, which explains the abnormal behaviour of sols on dilution towards coagulation by ions.

Chemical Laboratory,
Allahabad University,
Allahabad.
April 22, 1926.

SEDIMENTATION OF COLLOIDAL PARTICLES*

BY FRED W. LAIRD

The varied opinions and the contradictory reports of the experimentalists as well as the antipodal conclusions of the theorists in regard to the theory of sedimentation are themselves sufficient incentive for further research in this field. Sedimentation, in as much as it is closely connected with Brownian motion, is included in the kinetics of colloidal behaviour and forms one of its most interesting divisions. When the expression is first heard, the mind immediately engages itself in the conception of spherical particles falling freely through a fluid medium. Names such as, Stokes, Cunningham, Smoluchowski, Einstein, and others are passed in review and with a résumé of their work, a deeper and more comprehensive understanding of the term is developed.

In the application of the above term to colloids, in addition to the ordinary force of gravity which is always acting, one is forced to think also of the diffusion force, corresponding to osmotic pressure, Brownian movement, repulsion or attraction due to electrical phenomena, light and heat convection disturbances, and any other conceivable forces which may be acting, to aid or impede the free fall of the particle.

If a point is considered subjected to the action of many forces in such a manner that the point does not move, the usual inference to be drawn, is, that the components of the acting forces balance one another. In an analogous manner when a suspended colloid particle is reduced to a state of statistical rest then it is safe to conclude that the sum of all the components of the acting forces is zero. To illustrate more specifically consider the case of sedimentation equilibrium.

By the term sedimentation equilibrium is meant the steady state attained when the force of gravity and the diffusion forces acting in the opposite direction just balance one another. Consider a column of a sol containing uniform sized particles with an arbitrary initial distribution. Each particle will have the force of gravity acting on it and the force of diffusion acting in the opposite direction tending to buoy up the particle. If the gravitation force exceeds the diffusion force, then the particle will experience a drift downward; if the diffusion force is the greater, then the particle will travel upward in the opposite direction. After some interval of time it is conceivable that, *ceteris paribus*, the two opposing forces might become equal. When such is the case, a steady state is obtained or the so-called sedimentation equilibrium has been reached.

Smoluchowski[1] pointed out, that quite likely there is a relation in sols analogous to the hypsometric law for gases which states that there is a certain

* Contribution from the Colloid Laboratory of the University of Wisconsin.

[1] Smoluchowski: Ann. Physik, (4) **21**, 756 (1906).

definite relation between the density of the gas and the height of the column of gas considered[1]. "Thus the particles in a dispersed system of sufficiently low concentration must, under the influence of gravity, arrange themselves as do the molecules of a gas under the same conditions." The law, corresponding to the hypsometric law, when modified for colloidal solutions takes the following form:—

$$n_2 = n_1 \cdot e^{-\frac{N}{RT}\cdot[4/3\,\pi r^3 \delta (x_2 - x_1)g]} \qquad (1)$$

in which "n_2" is the number density of particles at a distance x_2, "n_1" is the number density of particles at a distance x_1; N is Avogadro's number; R and T have their usual significance; δ is the effective density; "g" is the force of gravity; "r" is the radius of the particle.

Perrin[2] was the first to test this law of more or less simple relations, experimentally, for dispersed systems and actually confirmed the predictions of Smoluchowski. His experiments were made with gamboge particles specially prepared by fractional centrifuging to obtain a sol of as nearly a uniform size of particle as possible. He actually determined, by counting, the number of particles per unit of volume at different levels ranging from 0-100μ from the surface. This is evidently a very small distance, but the agreement attained was rather remarkable. Other workers such as Zangger[3] and Brillouin[4] have done similar work with satisfactory results.

Westgren[5], working with gold sols containing particles considerably smaller than the others, namely about 21$\mu\mu$, and working at greater depths, was able to extend the work to distances of 1100$\mu\mu$ (1.1 mm). His agreement was much better than that of Perrin's due, probably, to different experimental technique. The work of Westgren means more than that of his pre-workers since the size of particle that he used was more nearly that demanded by the classical laws upon which the theory and its deductions were founded. From the work referred to above it would be inferred that equation (1) was found to hold rather well for the cases studied.

More recently however there has appeared an article by Mason and Weaver[6], entirely mathematical and theoretical, investigating the manner in which the steady state is attained. This theory assumes: (1) gravitational drift given by Stokes' law; (2) Brownian movement due to molecular bombardment; (3) a distribution of particles of the same size. The solution is complicated however; but, for the case of a uniform initial distribution, the authors are able to obtain a reduced form of the solution containing but one parameter. On plotting this one parameter family of curves, the density

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[1] Hatschek: "Physics and Chemistry of Colloids". 5th ed., page 36.
[2] Perrin: Compt. rend., **147**, 969 (1908).
[3] Kolloid-Z., **7**, 216 (1911).
[4] Ann. Chim. Phys., (8) **27**, 412 (1912).
[5] Z. physik. Chem., **89**, 63 (1914).
[6] Phys. Rev., (2) **3**, 412-26 (1924).

distribution at any time for a solution of any depth, density, viscosity, and for any size of particle, is obtained. The modified form of the equation is as follows:—

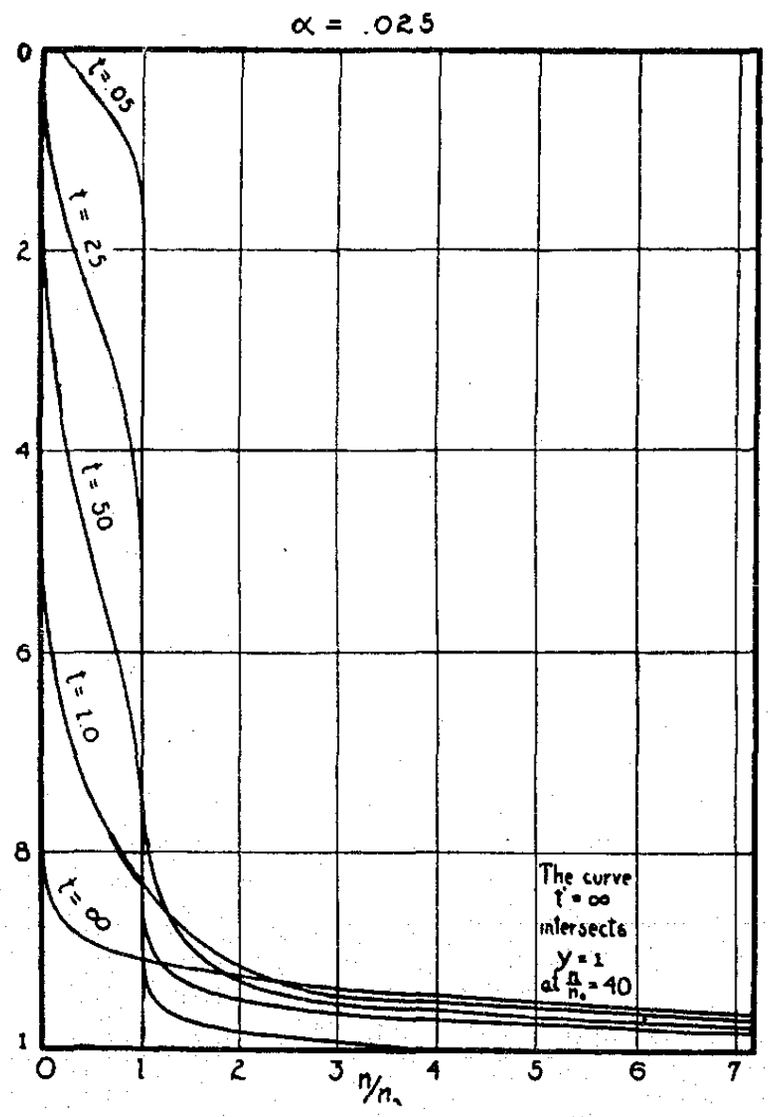


FIG. 1
Copied from article by Mason and Weaver: Phys. Rev., (2) 3, 418 (1924).

$$\frac{n}{n_o} = \frac{e^{y/\alpha}}{\alpha(e^{1/\alpha}-1)} + 16\,\alpha^2\,\pi\,e^{(2y-t')/4\alpha} \sum_{1}^{\infty} \frac{e^{-\alpha m^2 \pi^2 t'} \cdot \left[m\,(1 \mp e^{-\frac{1}{2}\alpha})\right] \cdot \left[\operatorname{Sin} m\,\pi\,y + 2\,\pi\,m\,\alpha \cos m\,\pi\,y\right]}{(1 + 4\pi^2 m^2 \alpha^2)^2}$$

where "n" and "n_o" are the density numbers of particles at different heights; R, T, N have their usual significance; μ is the viscosity of the solution; "a" is the radius of the particle; "X" is the gravitational force per particle; "t" is the time in seconds; "m" is the parameter; "y" is the fraction of the tube length considered governed by y = x/l where "x" is the depth below the surface and "l" is the length of the tube; $\alpha = A/Bl$; $l/B = \beta$; $\beta t' = t$,

$$A = \frac{RT}{N6\pi\mu a}; \quad B = \frac{x}{6\pi\mu a}$$

Through the use of this equation the work of Perrin referred to was analyzed, and using his data, it was shown that he waited the theoretically required time for his systems to come to equilibrium before he made his determinations.

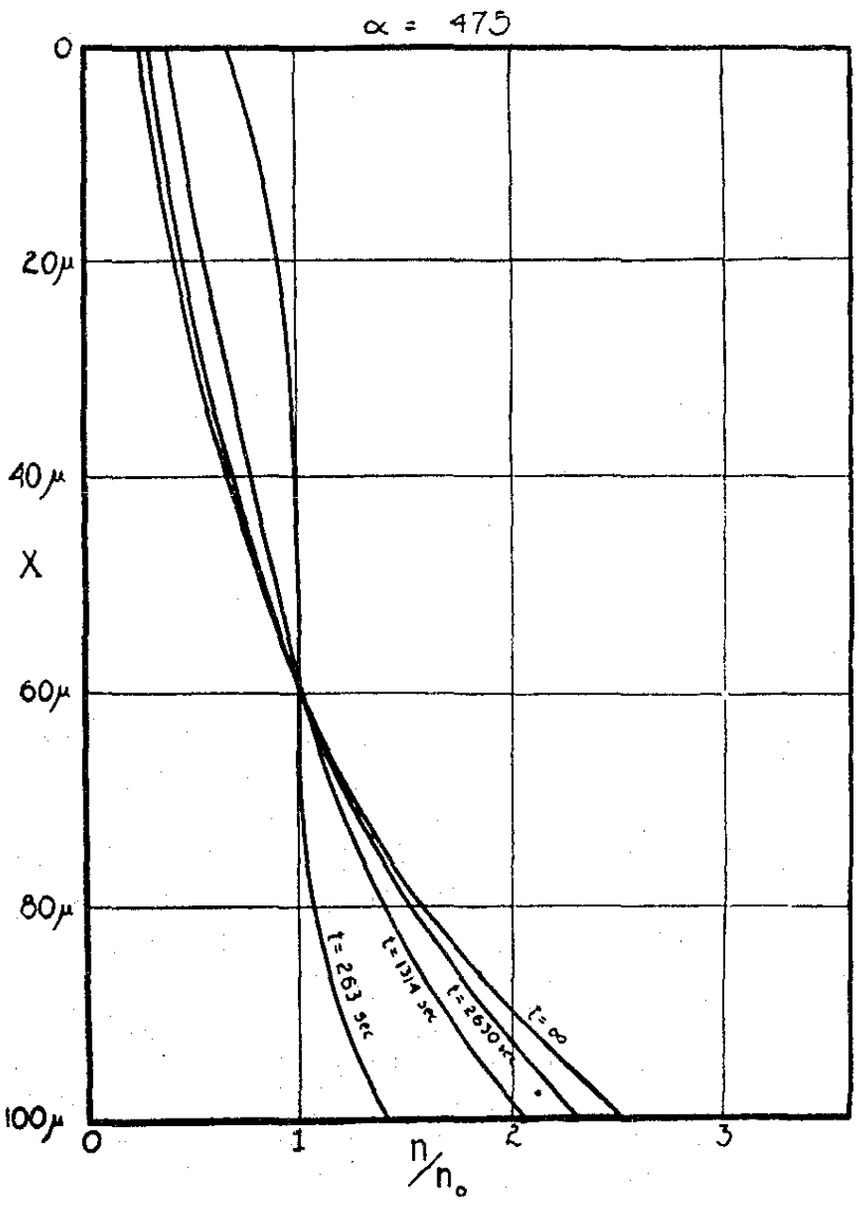


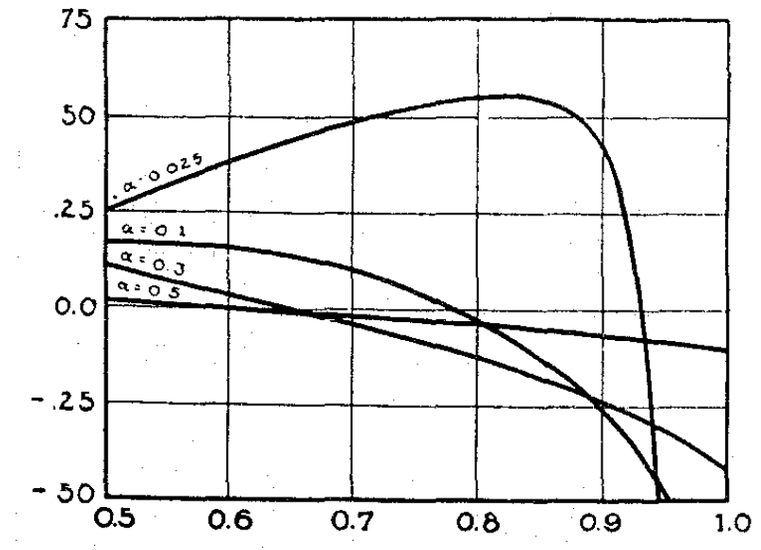
FIG. 2
Copied from article by Mason and Weaver: Phys. Rev., (2) 3, 423 (1924).

For values of α around 0.025 to 0.5 the curves shown in the paper (Figs. 1 and 2) for "t'" = 1 coincide sensibly with the curves for "t'" = ∞ so that it seems reasonable to assume that the steady state is reached in such cases when "t'" = 1 or actually when the time is $\beta t'$ seconds. This is for fairly large values of "α" which means small values of "l".

In order that this equation might be adapted to other types in which the values of "α" were not so large (cases where "l" is large) Weaver[1] investigated

[1] Phys. Rev., (2) 27, 499-503 (1926).

this case mathematically (case in which "α" has a value of the order of 2×10^{-6}) In the case of small values of "α" the magnitude of the transient term increases and therefore the time to set up the steady state increases. (Fig. 3). On account of the small values of "α" "the actual calculation of the sum involved is prohibitively laborious, since many hundred terms must be used to obtain a value of "n" for a single value of "x" and "t". An upper limit to the transient term may, however, be easily calculated.————————calling the transient term H(y,t')———this reduces to $H(y,t') < \frac{16\alpha}{\pi t'} \cdot e^{\frac{2y-t'}{4\alpha}}$. On



The magnitude of the transient term at $t' = 0.5$. The abscissas range from $y = 0.5$ to $y = 1.0$, and thus correspond to the lower half of the tube

FIG. 3
Copied from article by Weaver: Phys. Rev., (2) **27**, 501 (1926).

account of the size of α, the exponential factor decreases with enormous rapidity towards zero as soon as "t" exceeds 2y; and thus, since "y" never exceeds 1, as soon as "t'" exceeds 2. For example

t'	Upper bound for H
2.0000	5×10^{-6}
2.0001	3×10^{-11}
2.001	2×10^{-59}

Since the curves drawn in the previous article show that as "α" ranges from 0.1 to 2.0 the steady state is more and more rapidly attained, being sensibly reached in the slowest instance by "t'" = 1.0; and since the above argument shows that for smaller values of α the steady state is sensibly attained for values of "t'" just exceeding 2, it is therefore possible to state in general that the steady state will in all cases be reached in that length of time necessary for one of the particles, moving with the velocity given by Stokes' law, to fall two tube lengths."

From the above extracts of Weaver's paper it is to be noted that theoretically sedimentation will have taken place and the steady state attained in

twice the time that it would take a particle governed by Stokes' law to fall a tube length. Thus if the size of particle in the system is known it is possible to calculate, within reasonable limits, the time one should wait before considering such a system from the point of view of testing sedimenation laws. However, as Weaver himself mentions, the development of his equation does not take into account any other acting forces than the two mentioned so that if other forces are acting which might influence the attainment of the steady state (such as electric charges) his equation is not applicable in the strictest sense.

The case in which the electric forces may be considered as playing their part in the completion of sedimentation will be taken up in the following pages.

It has just been seen that there are theoretical and practical justifications for admitting the existence of a sedimentation equilibrium. However there are other writers who would attempt to show that the law is not as universal in its application as one might be led to suspect.

Among these is Burton[1] who points out that the formula would require that the concentration increase enormously as the bottom of the containing vessel is approached. Such large concentrations do not become apparent in practice. The ratio of the concentrations demanded by the equation at any two levels one cm, apart would be given by $\log \frac{n_2}{n_1} = 5000$ which according to Burton is out of all reason to one familiar with such silver suspensions.

Svedberg[2] criticized Burton's technique. In addition it is quite possible too that the quantities to be weighed were small and that therefore the small differences that perhaps may have been present were not apparent. It is also conceivable that the sols examined were not uniform and that therefore the sizes and distribution were such that the concentration at different levels was apparently the same.

Burton however, is not alone in this field. Porter[3] used a cell 5 mm in height and also studied the distribution of the number density of particles in gamboge suspensions and found that after a depth of 0.1 mm from the surface the hypsometric law did not hold. At greater depths than this the concentration apparently became constant. His conclusion was that certain forces exist between the particles which prevent the establishment of the equilibrium.

In the original derivation of the laws nothing was said about the forces which might exist between the colloidal particles due to their electric charges for they are based on the classical kinetic theory of matter. Consequently Burton[4] and Porter both saw fit to modify the original Perrin equation to fit their postulations. "Since these particles bear like charges they will repel one another; in fact, long continued observation of such particles by means of the ultramicroscope does not show collisions taking place between the particles at all. In introducing a correcting term in Perrin's equation to take

[1] Proc. Roy. Soc., **100A**, 414 (1922); Phil. Mag., **47**, 721 (1924).
[2] "Colloid Chemistry" (Wisconsin Lectures), 101 (1924).
[3] Phil. Mag., **44**, 641 (1922).
[4] "Physical Chemistry of Colloidal Solutions", 2nd ed. page 87.

account of this electrical repulsion, we have to calculate the electrical force on the particles in the layer, "dh" in thickness, due to the rest of the solution. Various approximations to the evaluation of this force suggest that it will be of the form "k.•n. e." per unit charge in the layer "dh", where "k" may be taken as a constant, at any rate for regions near the surface, and "e" is the charge in electrostatic units of each particle—we get "n" by the equation

$$n = \frac{c}{B + ke^{-c/A \cdot h}} \text{ in which } k = \frac{c - Bn_o}{n_o} \text{ and } A = \frac{RT}{N}\text{; } B = ke^2 \text{ and } c = v.(d-w)g = \text{effective gravitational force.}$$

In this equation for "n" for large values of "h", the value of "k" is small and can be neglected."

The above equation can be put in the same form as that of Perrin's but it then holds only for short distances near the surface or, in other words for small values of "h". ("h" being the distance below the surface that is considered.) The equation developed by Burton fits his own data and that of other investigators so far presented.

Porter and Hedges[1] have obtained, by reasoning that the gas law considerations applied to true solutions are also applicable to a gamboge suspension, an expression

$$\log_e \frac{n}{1-bn} + \frac{1}{1-hn} = ky + A$$

where A is the constant of integration which can be expressed in terms of (the unknown) concentration when $y = o$; b is a constant, "n" is the number of particles per cc; K is another constant dependent on g, N, R, T, mass of particle, and shrinkage of system, etc., and has a value of 121 in the work for which it was derived. ($b = 10.2 \times 10^{-8} cm^3$). The graph of such an equation fits also the experimental data of Burton, though both Porter's and Burton's curves do not coincide by any means with that plotted for the case of gaseous systems. Porter and Hedges[2] sum up their conclusions by saying that "it would appear from these preliminary determinations that there are in reality three regions in a suspension to which particular names might be given. In the first place, there is a very thin layer close to any surface in which there may be a special value for the mean concentration. This is the layer discussed by Willard Gibbs, and has been called after him. Its thickness is of the order of the range of inter molecular forces. Secondly, there is the layer studied by Perrin "inférieure au dixième de millimètre," in which the change of concentration of a suspensoid can be calculated from an application of the laws of gases in an analogy to that in which the change of pressure of an atmosphere is calculated. This is the Perrin layer. Thirdly there is a layer of one or two mm. thickness (in particular the cases studied in this paper) in which a further change of concentration occurs which cannot be calculated in the way adopted by Perrin. This merges gradually into the main body of the suspension, throughout which the concentration is sensibly uniform."

[1] Phil. Mag., **44**, 650 (1922).
[2] Phil. Mag., **44**, 650 (1922).

Bancroft[1] criticizes the summary of Porter thus "This is a possible way of looking at things but there is not much to recommend it if Burton's equation describes, as it seems to, the second and third layers of Porter's classification."

Svedberg[2] stated that in the case of Porter's experimental work it was quite likely that the sols had not reached equilibrium since Porter does not state how long he waited before making his measurements and that also the temperature was not sufficiently well controlled to allow the particles to reach a true sedimentation equilibrium. This point will be referred to later.

Experimental

The following experiments were conducted with the object of either showing Perrin's distribution law to be applicable over longer ranges or else confirming the work of other investigators.

Adopting Burton's method of attack, tubes of seasoned Pyrex 25 cm. in length and 5 cm. in diameter with side arms, were set up under protective coverings. For side arms, these tubes had portions of the side drawn out to a point as short as possible and sloped down so that when the tip was broken, the liquid could run out with the minimum disturbance. Though narrow tubes would have been preferable for the avoidance of convection currents, the above tubes were selected so that the volume of sol contained in each level, determined by the side arms, would be of sufficient quantity to analyze.

To minimize vibrations, the tubes were strapped to a heavy block of wood which in turn was fastened to a slab of concrete resting on a bed of loose sand in a basement room. A bowl of mercury when placed on top of the block showed no vibrations on its surface. The tubes were completely surrounded by lagged coverings to cut down temperature gradients as much as possible and also to afford protection from the light.

The sols used were of mercury dispersed in conductivity water by subjecting two streams of that element to the disintegration force of 500 volts D.C. in an electrical set-up recommended by Svedberg[3]. This sol was then partially fractionated by centrifuging and sedimentation to exclude the extra large particles. To prevent coagulation of the particles after the sol had been prepared, potassium citrate was added until the concentration was 0.0025N with respect to the citrate. Such sols were very stable and of a dark brown color.

It has been suggested that sols prepared by the Bredig method are high in oxide content[4]. These sols were examined for mercuric oxide, samples were analyzed by the Hulett method[5]. They showed on the average about 37% oxide calculated on the basis of total amount of mercury present. On ac-

[1] "Applied Colloid Chemistry", 164 (1926).
[2] "Colloid Chemistry", 101 (1924).
[3] Svedberg: "Colloid Chemistry" (Wisconsin Lectures), 40 (1924).
[4] Freundlich: "Colloid and Capillary Chemistry", 512 (1922).
[5] Z. physik. Chem., **37**, 401 (1901).

count of this fact the effective density and solubility of mercuric oxide should be taken into account before determining the exact size of particle present[1].

The concentration of the particles in the different levels was obtained by taking the sol in these levels after they had been allowed to sediment and actually counting the particles in the ultramicroscope in a given optical unit of volume. These counts were taken systematically, at equal times, so that if necessary they could be used in statistical calculations such as fluctuations and compressibilities. This was accomplished by means of a rotating constant-speed, red celluloid disc with a small white sector through which the white light from a bright light filament passed once per revolution. Thus when the field in the eyepiece, which had to be decreased by means of a diaphragm in order to limit the number of particles visible at one time, appeared white, a count of the total number of particles was taken and recorded. This was done for several hundred counts and the average number of particles per unit of volume computed. By keeping the optical set-up the same, the relative number of particles per unit of volume per different level could be obtained. From the analysis of the mercury the approximate average size of particle left in suspension could be determined.

The analysis of the mercury content had to be made colorimetrically on account of the small amount of mercury present in the sol after sedimentation and also because the volume of the sol in each level was small. The amount of citrate present too, was of the same order of magnitude as the amount of mercury. Thus gravimetric methods were excluded. The method used was one recommended by P. Ménière[2] which depends on the intensity of the blue color formed when diphenyl carbazide reacts with a nitrate solution of mercury. This method is used with most success when the quantity of mercury present is small, which is the case in the sols used. The color comparisons were made by means of a Bausch and Lomb Duboscq type colorimeter.

Results.

EXPERIMENT 1

Time of sedimentation 65.6 days. Length of sedimenting column 22.0 cm.

No. of level	Distance of level from surface cms.	Average No. particles per unit of vol.	Total No. of counts
1	5.8	1.14	1179
2	10.8	1.12	491
3	15.6	0.905	565
4	20.6	1.12	1216

[1] When mercury, boiled conductivity water, and diphenyl carbazide are shaken up together no coloration of the indicator is observed. If, however, sols are prepared either by the arc method, the disrupting of mercury lamella by allowing mercury to fall through a vertical height and impinge under water against the sides of a glass vessel, or by forcing water up under the surface of mercury, and if diphenyl carbazide is added, a deep blue coloration of the indicator is observed, its intensity varying with the time of preparation. Since no coloration of the diphenyl carbazide in the first case is taken as an indication that no soluble mercuric compound is formed and since it is known that a solution of mercuric oxide affects the indicator, it is therefore concluded that in the other cases slight amounts of mercuric oxide are formed.

[2] Compt. rend., **146**, 754 (1908).

EXPERIMENT 2

Time of sedimentation 84.08 days. Length of sedimenting column 21 cms.

No. of level	Distance of level from surface cms.	Average No. particles per unit vol.	Total No. of counts
1	3.9	0.64	406
2	8.4	0.92	426
3	12.4	1.68	367
4	17.0	0.766	460

EXPERIMENT 3

Time of sedimentation 276 days. Length of sedimenting column 24 cms.

No. of level	Distance of level from surface cms.	Average No. particles per unit vol.	Total No. of counts
1	6.2	1.76	4343
2	10.0	——	——
3	14.3	1.14	926
4	18.3	——	——
5	22.0	1.34	1225

From the determination of the amount of mercury, calculations indicate that the radius of the particle present in suspension after sedimentation is of the order of $8.3\mu\mu$ (8.3×10^{-7}cm.) In the computation of this size of particle no account was taken of the fact that mercuric oxide is soluble and that therefore, the total amount of mercury determined in the analysis was not just the suspended mercury. However mercuric oxide is less dense than mercury so that it would take a larger particle of mercuric oxide to fall the same distance in the same length of time. These two considertions are working against one another but should be taken into account if more than an approximate size of particle is desired.

From the three tables given it is evident that the concentration of the particles in the mercury sols studied did not change appreciably on standing in the different levels. The number of particles in the different levels in experiment 1 are practically constant. Consequently in this case one would most certainly say that the distribution law was not applicable, for the data are analogous to those of Porter and Burton. The first three levels in experiment 2 seem to be progressing favourably but level four is decidedly out of place, but is just as probable as the value for say the third level. The average number in experiment 3 is fairly constant and in agreement with the first experiment. It is to be noted in all cases that sufficient counts were taken in order to get a good representative value for the average number of particles. To see if the law similar to that of van der Waals can be applied, it is possible to compute with the aid of data which go to make up the total number of counts, the ratio of the so-called compressibility of colloidal solutions, β/β_0 which is a measure of the variation of the sols from the Boyle-van't Hoff laws. The phase of compressibilities and fluctuations however will not be dealt with here at this time.

After this experimental work had been completed and written, another theoretical paper appeared on the same identical problem as that solved by Weaver. Since this paper contains no mention of Weaver's work and also since it has more drastic conclusions than that of Weaver's, it seems that attention should be called to the apparent discrepancies.

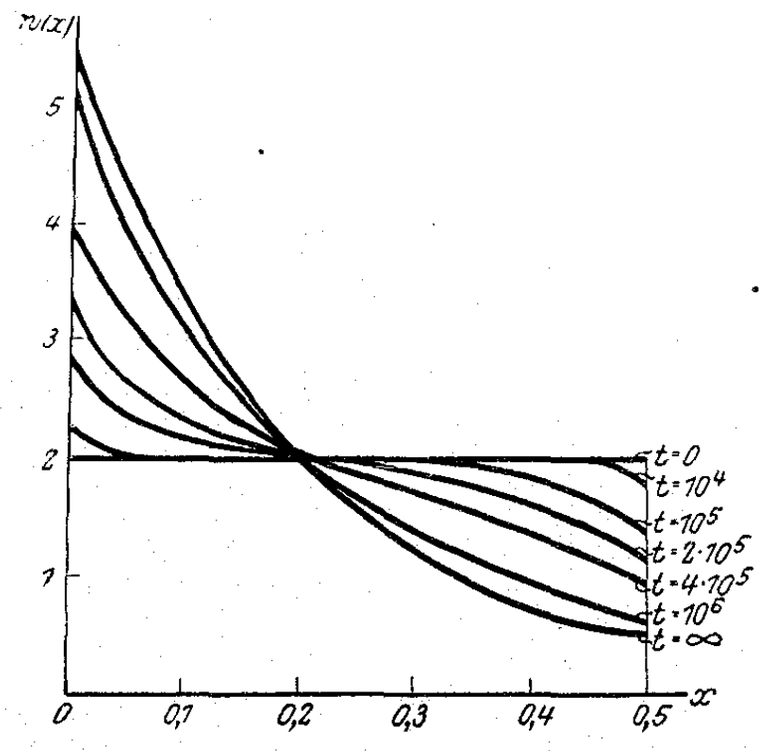


FIG. 4
Copied from article by Fürth: Z. Physik, 40, 5, 351 (1926).

By similar assumptions as Weaver, Fürth[1] arrives at an expression for the density distribution of the particles in terms of x and t namely,

$$w(x_1t) = 32D^3\pi^2.c.e^{-\frac{CX}{2D}-\frac{C^2t}{4D}}\sum_{n=1}^{\infty}\left\{\left(\frac{n}{C^2H^2+4\pi^2D^2n^2}\right)^2 e^{-\frac{\pi^2Dtn^2}{H^2}}\left[(-1)^n e^{\frac{CH}{2D}}-1\right]\right.$$

$$\left.\left(\cos\frac{\pi\times n}{H}-\frac{CH}{2D\pi n}\operatorname{Sin}\frac{\pi\times n}{H}\right)\right\}+\frac{C}{D}\cdot\frac{1}{1-e^{\frac{-CH}{D}}}\cdot e^{\frac{-CX}{D}}.$$

which when $t = \infty$ reduces to $w(x,\infty) = \frac{C}{D}\cdot\frac{1}{1-e^{\frac{-CH}{D}}}\cdot e^{\frac{-CX}{D}}$

In the above equation, w(x,t) is the number distribution at a height x and a time t; D is the diffusion coefficient (about 4×10^{-8} in c.g.s. units); c is the velocity of the convection stream (about 2×10^{-7} c.g.s. units); n is a parameter; H is the height of the column of the tube or cell. This expression is

[1] Fürth: Z. Physik, **40**, 5, 351 (1926).

analogous to Weaver's equation and as his does, also contains a transient term. To demonstrate the use of it Fürth considers two cases: for a small size of particle, and then for one twice the size. Thus, if H = 0.5 cm. c = 2×10^{-7}; D = 4×10^{-8} for one case of particle size and H = 0.5 c = 8×10^{-7} and D = 2×10^{-8} for a second case in which the particle is twice the size of the first, then Fürth obtains two families of curves by substituting these values in his equation and these are shown in Figs. 4 and 5. These curves are of the same general nature as Weaver's (Figs. 1 and 2). Fig. 4 shows that

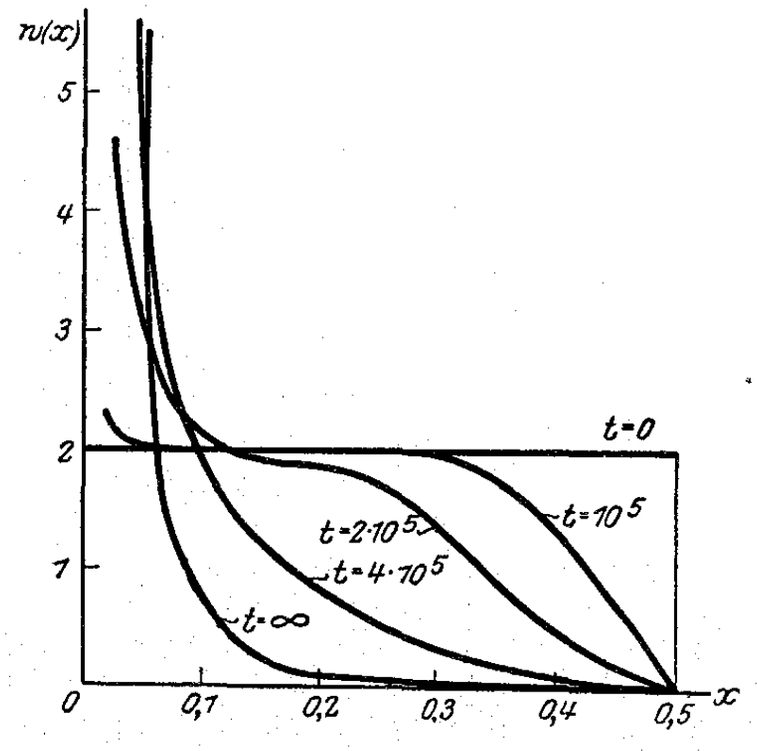


FIG. 5
Copied from article by Fürth: Z. Physik, **40**, 5, 351 (1926).

when t = 2.5×10^6 seconds (time required for particle to fall one H) the equilibrium is almost established (e.g. curves t = 10^6 and t = ∞ almost coincide). This is the case in which *c* is small and D is large. When *c* is large and D is small then the result is as indicated in Fig. 5 and shows that for a value of t = 6×10^5 (time required to fall one H in second case) there is still considerable deviation in the sedimentation equilibrium for this time. Furthermore it can be seen that the equilibrium is closer to the bottom of the containing vessel and in such a way that "Im extremen Fall sehr grosser Fallgeschwindigkeit und sehr kleiner Diffusion findet die Sedimentation so statt, dass die gelöste Substanz im Lösungsmittel gleichmässig herabsinkt, und zwar so, dass sich zwischen den bei den eine fast scharfe Trennungfläche ausbildet, die mit der konstanten Geschwindigkeit *c* herabsinkt—".

Fürth recommends that before observations on sedimenting systems are begun, one should calculate by means of his equations the theoretical time required for equilibrium to be attained. Thus in the case of spherical gamboge

particles of radius 7×10^{-6} cm, in case one discussed by him, and of 14×10^{-6} in case two, if the vessel is 0.5 cm height, the time required by calculation is 10^6 seconds or 11 days.

The influence of height of the vessel on the time "t" is approximated by means of the exponential $e^{\frac{-\pi^2 Dt\, n^2}{H^2}}$ and the time is thus proportional to H^2. Thus if H = 0.1 mm the time of equilibrium would be 400 seconds or 7 minutes. If H = 1 metre then t = 1400 years.

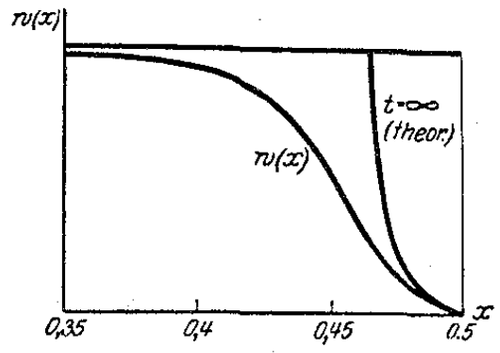


FIG. 6
Copied from article by Fürth: Z. Physik, **40**, 5, 33 (1926).

Thus Fürth points out that, in shallow vessels, sedimentation equilibrium is attained rapidly, while in deep vessels the time is much greater or, as he says, is so great "dass die Sedimentation selbst dann nicht beobachtbar wird, wenn absolut keine äussern Störungen eintreten würden—dass wir bei genügend kleinen Teilchen eine Sedimentation überhaupt nicht eintreten sehen, wie übrigens auch von anderer Seite bereits hervorgehoben wurde."

Fürth's criticism of Porter's work is that, since calculations show that eleven days were required, Porter did not measure a state of equilibrium but rather, that state which precedes it, (Fig. 6). Consequently Fürth is inclined to waive Porter's conclusion, i.e., that a law analogous to van der Waals' holds, which takes into account the mutual repulsion of the particles.

Fürth also examined Burton's work, in which Burton used a tube 145 cm long containing colloids of gamboge, silver, copper and arsenic trisulphide, and calculated that the times required for sedimentation in these cases, were of the order of 1000 years.

Having thus reviewed Fürth's paper we are in a position to compare Weaver's solutions with those of Fürth's. From Fürth's calculations it is evident that if "t" is proportional to H^2, then the proportionality factor is approximately 4×10^6. Now consider the case of Burton with the 94 cm. tube. The approximate length of time required would then be: if $t = kH^2 = \frac{4\times10^6\times(96)^2}{3600\times24\times365} = 1120$ yrs. For this same problem Weaver offers a solution of 37 days. However in the above calculation the radius used by Weaver was approximately 1.7×10^{-5} cm. while that used in the given calculation, as Fürth used, was 7×10^{-6} cm.

In the light of Weaver's theory, equation, and deductions, the time required to fall twice the length of a tube is that time required for sedimentation equilibrium to take place. Thus if the depth of the cell is 0.5 cm. and the radius is 7×10^{-6} cm. and if the cell is filled with gamboge suspension, then since by Stokes' law $V = \frac{2g(d_2-d_1)a^2}{9\mu}$ and since $S = vt$ where S is the tube length in cms. and "t" is the time in seconds, then it follows that $t = \frac{S}{V} = \frac{9S\mu}{2g(d_2-d_1)a^2} = 2.3\times10^6$ seconds or 27 days which is the time required to fall one S. Therefore to fall 2 S it would require 54 days. Thus by this calculation one could say also that insufficient time had been allowed by Porter before making his observations.

In the case of Burton's work where the 145 cm. tube was filled with a suspension of gamboge, if the particles were 7×10^{-6} cm. in radius then "t" by Weaver's reasoning would be 43.0 years. If the same tube was filled with copper suspension and the particles were of the same size then "t" = 1.08 years. In either case, by this calculation, Burton did not allow sufficient time for his systems to reach equilibrium since he waited but four months.

It is thus apparent when one compares the two solutions offered for the same problems that they do not check in actual values though both suggest (except in the case where the sol considered was copper and the size of particles taken as 1.7×10^{-5} cm.) that sufficient time had not elapsed before the observations were made. Thus the two solutions, though of practically the same form, do not give the same results. That both authors have analogous solutions may be seen by inspecting the curves of Figs. 1 and 5 for it can readily be seen that if Fürth's curves be plotted on different axes and with different scales the practically identical curves of Weaver may be obtained. This would indicate then that one of the authors has misinterpreted the conclusions to be drawn in regard to which factors influence most the attainment of the steady state. That is, either Furth's approximation of $e^{\frac{-\pi^2Dtn^2}{H^2}}$ or the upper boundary of Weaver's transient term $H(y,t') < \frac{16\alpha}{\pi t'}\cdot e^{\frac{2y-t'}{4\alpha}}$ is in error.

In connection with the problem of sedimentation of particles and Fürth's statement that some particles may never settle, it is interesting to note the variance of opinions in regard to the so-called limiting size of particles. In order to have some tangible conception of the minimum size that a particle must have before it will not fall in a liquid, Burton[1] equates the value of the mean square displacement of a particle to the distance a particle would fall if allowed to fall freely in a unit of time. This is equivalent to saying that at some unit of time the vertical component of the Brownian movement is equal

[1] Alexander: "Colloid Chemistry", 1, 166-7 (1926).

to the distance of free fall of the same particle. If such is the case then we have for the mean square displacement the following equation $\bar{D}^2 = \frac{RT}{N} \cdot \frac{t}{3\pi n} \cdot \frac{1}{a}$. The velocity of fall is given by Stokes' law $v = \frac{2(d_2-d_1)ga^2}{9n}$ from which the distance of fall in a unit of time is given as vt. Equating and solving for "a", the so-called critical radius, we get $a^5 = \frac{81RTn}{12\pi N(d_2-d_1)^2g^2t}$. It is thus seen that

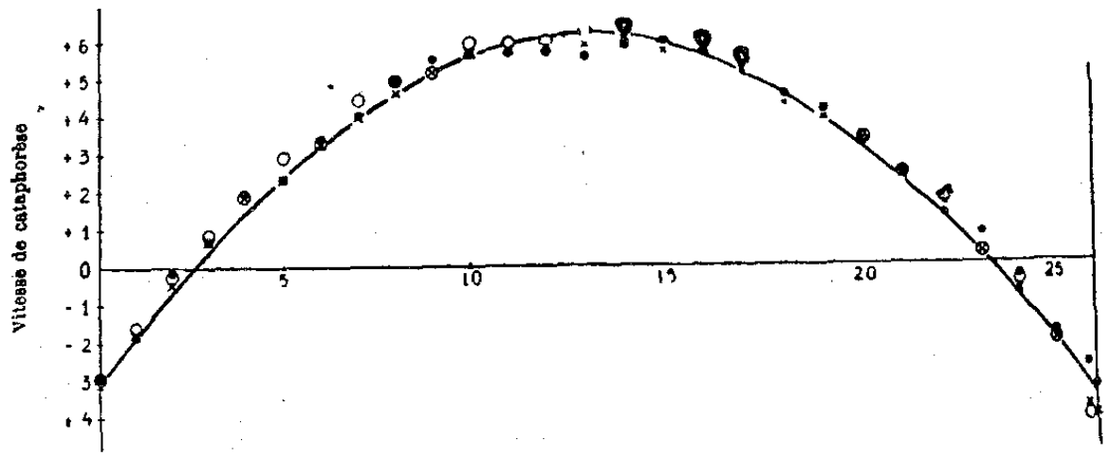


FIG. 7
Epaisseur de la cuvette. Unité 40 μ
Copied from article by van der Grinten: J. chim. phys., 30, 3, 228 (1926).

"a" is dependent on "t" and varies inversely with $\sqrt[5]{t}$. If now values are substituted in the above equation for some sol such as silver which has an effective density of 10, and taking "t" as unity, we get for "a" a value of 2.4×10^{-5} cm. This value, according to Burton, is, within certain limits, a criterion for its sedimentation. Since however "a" depends on "t" there is some doubt about the value of "t" which should be used, for obviously it will make considerable difference. In regard to this point, consider the work of van der Grinten[1]. The author is endeavoring to determine whether the particle attains its limiting velocity immediately or after the expiration of a sensible length of time during cataphoresis. If Brownian movement, gravity, and cataphoresis do not all exert constant effects, any discrepancy will show up if the velocity of cataphoresis is not shown to be of a constant nature. Thus he says, "Il est très important de savoir si la vitesse que prend une particule reste constante dès le premier moment où l'on établit le courant. On voit sur la figure 5 trois courbes, [Fig. 7] dans lesquelles la vitesse des particules sont mesurées immédiatement après la fermeture du courant, 10 secondes après et 30 secondes plus tard. On voit qu'il s'établit dans la cuvette un état stationaire pendant un temps qui est pour nos recherches négligeable." Thus the speed is identical at all three times, so that the

[1] J. Chim. phys., 30, 3, 228 (1926).

particle under the influence of the three forces experiences the same resultant effective velocity at the beginning of the experiment as it does at the end. Consequently it seems probable that the unit of time, one second, is sufficient, though as Burton points out, this time limit can not be reduced indefinitely.

Ayres[1] puts Perrin's law in the form of $\log_e \frac{Co}{Cx} = mgkx$ where Cx is the concentration at the height x, "m" is the mass of the particle, "g" is the acceleration due to gravity, and "k" is a constant equal at a normal temperature to 3.10^{13} in c.g.s. units. Thus if "d" is the density of the particle then $m = 4/3\pi r^3 d$ then $mgk = 10^{17} r^3 d = \alpha$ and when $\alpha = 1$, $r^3 d = 10^{-17}$. Now Ayres has previously shown that complete subsidence may be assumed to be attained if $\alpha = 10$. Hence $r^3 d = 10^{-16}$. This equation is the criterion for subsidence and when $r^3 d$ is less than 10^{-16} complete subsidence is impossible.

Now suppose the sol is silver and the effective density is 10 then $r^3 = 10^{-17}$ or $r = 2.1 \times 10^{-6}$ cms. This value is only 0.1 as large as that suggested by Burton. Only when $\alpha = 10{,}000$ does the value of "r" by this method approach that given by Burton. Then $r^3 d = 10^{-13}$ and if $d = 10$, $r^3 = 10 \times 10^{-15}$ and therefore $r = 2.2\ 10^{-5}$ cms. Thus there is some discrepancy between the two methods, but the latter method of Ayres, on the surface, seems to be more nearly applicable to practical cases. However the terms "incomplete" and "complete subsidence" are somewhat vague. A case of complete subsidence might mean that state in which a sedimentation equilibrium had been attained or else that condition in which particles were of such a size that they would finally settle to the bottom of the containing vessel.

The problem of sedimentation equilibrium studies was suggested by Dr. E. O. Kraemer.

Summary

1. Conception of sedimentation equilibrium has been discussed in the light of the work by Perrin, Westgren, Burton, Porter and Hedges.

2. Additional data have been presented on sedimentation equilibrium yielding results similar to Burton and Porter and Hedges.

3. The theoretical papers of Mason and Weaver, Weaver, and Fürth have been reviewed and compared.

4. Discrepancies between existing methods for the calculation of critical radii have been discussed.

Madison, Wisconsin.

[1] Alexander: "Colloid Chemistry", **1**, 856-7 (1926).

A STUDY OF THE TERNARY SYSTEM METHYL BENZOATE, METHANOL, WATER*

BY E. C. GILBERT AND B. E. LAUER

During the course of an investigation along other lines it became necessary to know the solubility relationships of the three liquids represented by this system and accordingly a careful study was made at three different temperatures to ascertain particularly the effect of rising temperature.

Materials

Methyl Benzoate—Chemically pure methyl benzoate, obtained from Eastman Kodak Company, was redistilled under reduced pressure, a fraction boiling between 88°C. and 91°C. at a pressure of 17 mm. being collected.

Methanol—"C. P. Special" dry methanol was redistilled, and a fraction collected which boiled between 64.7°C. and 64.8°C. at a pressure of 760 mm.

Water—Freshly distilled water was used throughout.

Apparatus and Method

The apparatus and method used were similar to those of Walton and Jenkins[1]. Starting with a measured quantity of one component in a large test tube in a transparent constant-temperature bath, the other two components were alternately added dropwise from calibrated burettes, which were provided with long extension tips running down into the test tube through the stopper. The mixture was stirred rapidly with a motor stirrer and the equilibrium end-point taken at the instant the solution became clear (with a lamp on the opposite side.) The end-points were sharp and easily duplicated for the most part. The temperature of the burettes was recorded, and from the density of the materials the weight was computed. The temperature varied very little during any run. The solutions were carefully protected from moisture. Several runs were made at 25°, 15°, and 35°C.

Overlapping portions of the curves obtained in different runs coincided exactly. The solubility of water in methyl benzoate and vice versa was determined at each temperature from the densities of the respective saturated solutions by assuming the mixture law to hold at the low concentrations involved. The density of all materials was determined with a Sprengel-type picnometer.

Results

A few representative results obtained are given in Table I, and the solubility isotherms for 15°C. and 35°C. are plotted in Fig. 1. The isotherm at 25°C. falls between these two and is omitted for the sake of clarity in the drawing.

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*Contribution from the Department of Chemistry, Oregon State College.

[1] Walton and Jenkins: J. Am. Chem. Soc., **45**, 2555-59 (1923).

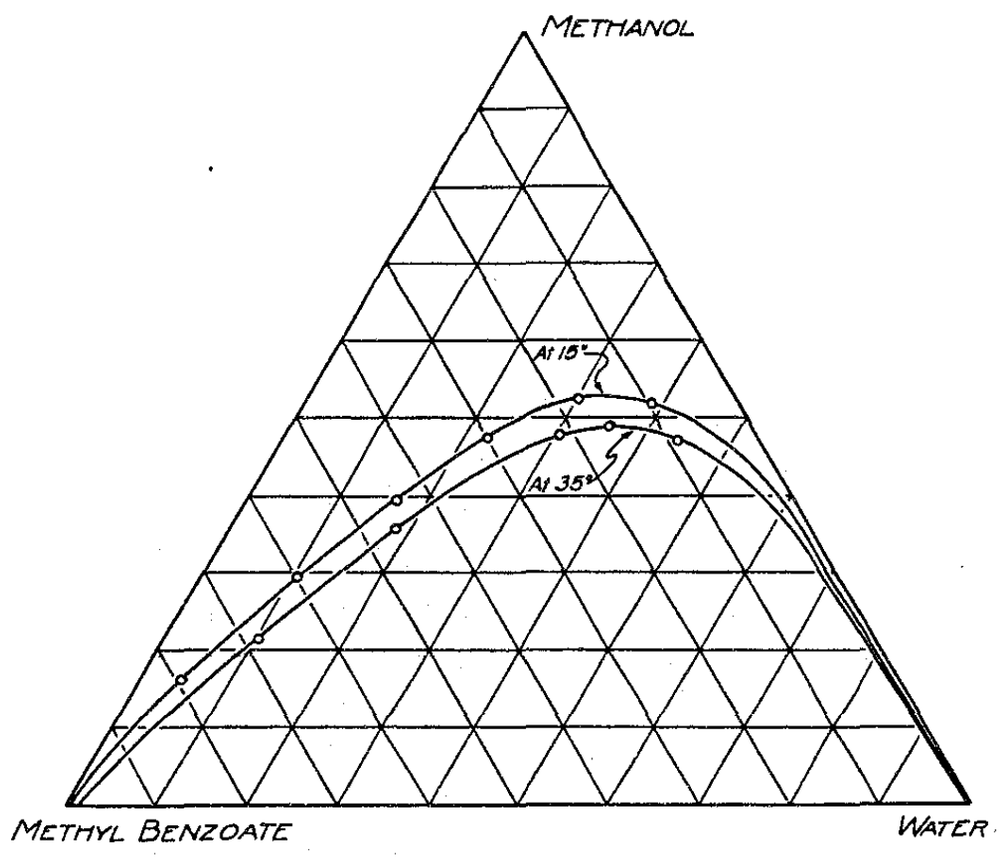


FIG. 1

TABLE I

Weight percentage of one-phase equilibrium mixtures along the solubility isotherms

At 15°C.		At 25°C.		At 35°C.	
% Ester	% Alcohol	%Ester	% Alcohol	% Ester	% Alcohol
99.8	0.0	99.4	0.0	98.8	0.0
79.4	16.1	83.8	12.4	68.3	20.9
75.0	19.4	74.1	19.2	62.4	25.0
60.0	29.3	65.8	24.5	59.9	26.9
44.0	39.3	54.4	31.7	51.7	32.3
34.5	45.1	41.3	39.4	45.8	35.7
29.9	47.4	30.0	45.4	39.8	39.1
23.1	50.6	23.9	48.0	32.7	42.7
17.3	52.6	17.8	49.8	28.0	44.9
14.5	52.4	14.0	50.6	21.7	47.8
10.7	52.0	11.7	50.6	18.0	48.6
0.1	0.0	9.5	50.3	15.2	49.2
		4.4	46.5	11.3	48.3
		2.2	43.6	8.9	47.0
		1.1	39.9	0.5	0.0
		0.4	0.0		

Discussion

Methyl benzoate and water are almost immiscible at ordinary temperatures and a considerable proportion of the alcohol is necessary to produce a one-phase mixture. The solubility surface rises abruptly and a twenty degree rise in temperature causes but little decrease in the amount of alcohol which must be used.

Bancroft and others[1] found in a number of similar systems that if the quantity of one component is kept fixed, an equation of the type,

$$X/Y^n = \text{constant}$$

represents quite well the resulting curve, where X is the amount of the second component, Y the amount of the third, and n is a constant.

This being the case log X plotted against log Y should give a straight line, since $X - n \cdot \log Y = \log K$, but when the equation was tested for the system here investigated an interesting fact was observed. If the weight of methanol is taken as Y and that of water as X for a fixed weight of methyl benzoate, the plot of log Y against log X is practically a straight line at 15°C., but at 25°C. the curve has become concave toward the X axis, and at 35°C. the concavity is quite pronounced. Agreement with the simple equation is therefore apparently dependent on the temperature.

Summary

1. The solubility isotherms of the ternary system methyl benzoate, methanol, water are given for 15°C., 25°C., 35°C.

2. The equation $X/Y^n = K$, fits the system very well at the lower temperature, but the divergence increases considerably with increasing temperatures.

Corvallis, Oregon.

[1] Bancroft: J. Phys. Chem., **3**, 217 (1899); Bonner: **14**, 738 (1910); Lincoln: **8**, 248 (1904).

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PHENOL TESTS. IV*

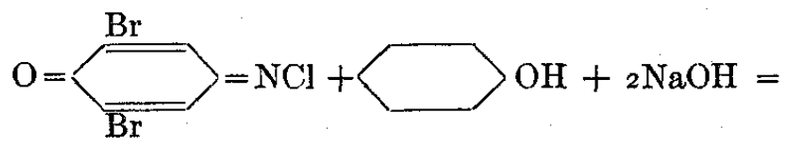
A Study of the Velocity of Indophenol Formation. 2, 6-Dibromobenzenoneindophenol.

BY H. D. GIBBS

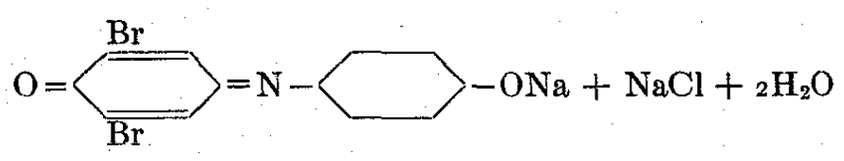
Introduction

In the third paper of this series a test for phenols was described. The test is based upon the reaction between a quinonechloroimide and a phenol forming an indophenol, the salt of which gives an intense blue solution. A special spectrophotometric study was made of the reaction between 2, 6-dibromoquinonechloroimide and phenol. On studying this reaction upon a quantitative basis enormous changes in the rate of the formation of the blue color were found to be dependent upon the pH of the solutions. Preliminary experiments failed to reveal any definite correlation or definite mechanism underlying the reactions producing the indophenol. Therefore, this systematic study was undertaken.

It has been found that a very definite and simple relation exists. This type of indophenol formation is usually represented by the equation[1]



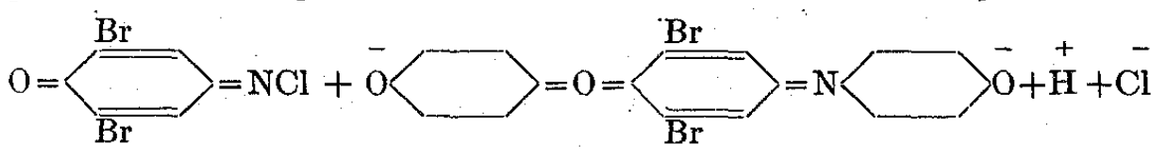
2,6-dibromoquinone-chloroimide — phenol



2, 6-dibromobenzenoneindophenol

While this equation correctly expresses the proportions of substances entering into the reaction, which might be considered of the third order, it does not represent the true underlying mechanism of the indophenol production.

It has been found that the reaction can be explained by assuming that the phenolate and the quinonechloroimide react in the sense of the equation

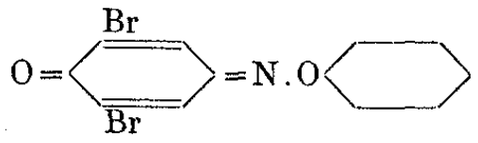


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* Senior Chemist, Hygienic Laboratory. Published by permission of the Surgeon-General, United States Public Health Service.

[1] The question of nomenclature will be fully discussed in a later paper entitled STUDIES ON OXIDATION-REDUCTION. XII. PREPARATION OF INDOPHENOLS WHICH ARE USEFUL AS OXIDATION-REDUCTION INDICATORS.

There is some evidence of the formation of the intermediate compound



which, in alkaline solution, rearranges to the blue salt of the indophenol. It seems most probable that this rearrangement is very rapid and is not the governing factor in the speed of indophenol formation.

Since, other things being equal, the speed of the reaction as expressed above is dependent upon the concentration of the phenolate, the effect of pH upon the speed of the reaction is clear, and in buffered solutions in the alkaline ranges in the presence of a great excess of phenol, the measurements of the velocity of the reaction, calculated according to the first order, should give a constant, which they do. The reaction is, therefore, under these conditions, pseudomonomolecular.

When the concentrations of the imide and of the phenol are more nearly equal, the velocity of the reaction, calculated according to the second order, gives a constant agreement with the values obtained in the former case.

The averages of 18 values obtained experimentally fix this value at 1.68×10^4.

It is interesting to note that technique has been developed by means of which the reaction can be followed and the velocity measured, with a fair degree of accuracy, at concentration so minute, that, heretofore, they have been below the limits of many of the available qualitative tests for phenol.

Fair results have been obtained with 1 part of phenol in 2 million. Some measurements of an unsatisfactory nature, were obtained with 1 part phenol in 20 million.

In the early experimental work great difficulty was experienced in obtaining consistent results and it was soon discovered that the temperature coefficient of the reaction is considerable. This necessitated the construction of reaction vessels in which the temperature could be accurately controlled. It was also found that the various buffer solutions employed should be standardized to a fair degree of accuracy under uniform conditions. The standardizations were made electrometrically for the same dilutions employed in the reacting mixtures. I have Mr. W. L. Hall to thank for the electrometric standardizations.

Mechanism of the Reaction

The reaction between 2, 6-dibromoquinonechloroimide and phenol in alkaline solutions may be represented as taking place in a number of ways. Since we have no evidence that indophenols form in acid solution (if they do form the rate is so slow that there is no evidence of the production of the red acid form), the first thought is to formulate a reaction of the third order as occurring between a = imide, b = phenol and c = hydroxyl.

In buffered solutions the concentration of the hydroxyl ion, "c", is constant and the velocity equation becomes

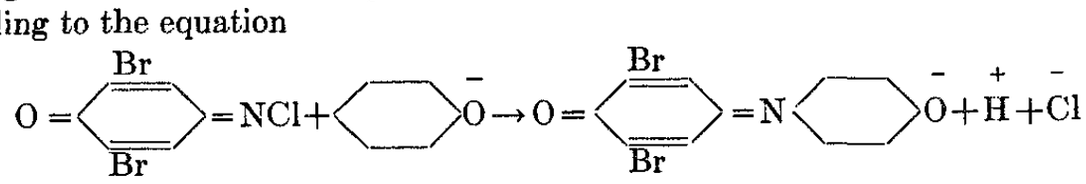
1. $$\frac{dx}{dt} = kc(a-x)\,(b-x)$$

which integrated gives

2. $$k = \frac{1}{tc\,(a-b)\,(b-c)} \ln \frac{b(a-x)}{a(b-x)}$$

No constant values for "k" are obtained by the use of this conception.

We are evidently dealing with a complex reacting solution, the first stage being the formation of the phenolate ion, which reacts with the imide according to the equation

3. 

imide phenolate indophenol ion

This reaction appears to be of the second order. When it is carried on in buffered solutions the concentration of the phenolate ion is determined by the pH of the buffer from the equation

4. $$pH = pKa + \log \frac{\alpha}{(1-\alpha)}$$

in which α is the ratio $\frac{\text{phenolate}}{\text{total phenol}}$.

The concentration of the phenolate ion is then the concentration of the total phenol times α.

In reaction "3" if "a" equals the concentration of the imide, "b" the original concentration of the phenol, "bα" the concentration of the phenolate and "(b−x) α" the concentration of the phenolate ion at any time, "t", the velocity equation becomes

5. $$\frac{dx}{dt} = k_2(a-x)\,(b-x)\alpha$$

which integrated gives

6. $$k_2 = \frac{1}{t\,\alpha\,(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$

or

7. $$k_2 = \frac{2.3026}{t\,\alpha\,(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

When the concentration of the phenol is very large in respect to the imide and when pH is high, the concentration of the phenolate ion becomes a constant for all practical purposes and the equation reduces to the form of a monomolecular reaction, the velocity constant of which is

8. $$k = \frac{1}{tb\,\alpha} \ln \frac{a}{(a-x)}$$

or

$$9. \qquad k = \frac{2.3026}{\alpha\ tb} \log \frac{a}{(a-x)}$$

While velocity equations 6, 7, 8 and 9 do not contain the OH^- concentration directly, it is evident that the concentration of phenolate ion, is dependent, not only upon the concentration of the total phenol, but upon this factor also.

Experimental

a. The Apparatus. All of the spectrophotometric measurements were made by means of a Keuffel and Esser color analyzer with the solutions held in 10 cm tubes. During the early part of the work it was not realized that

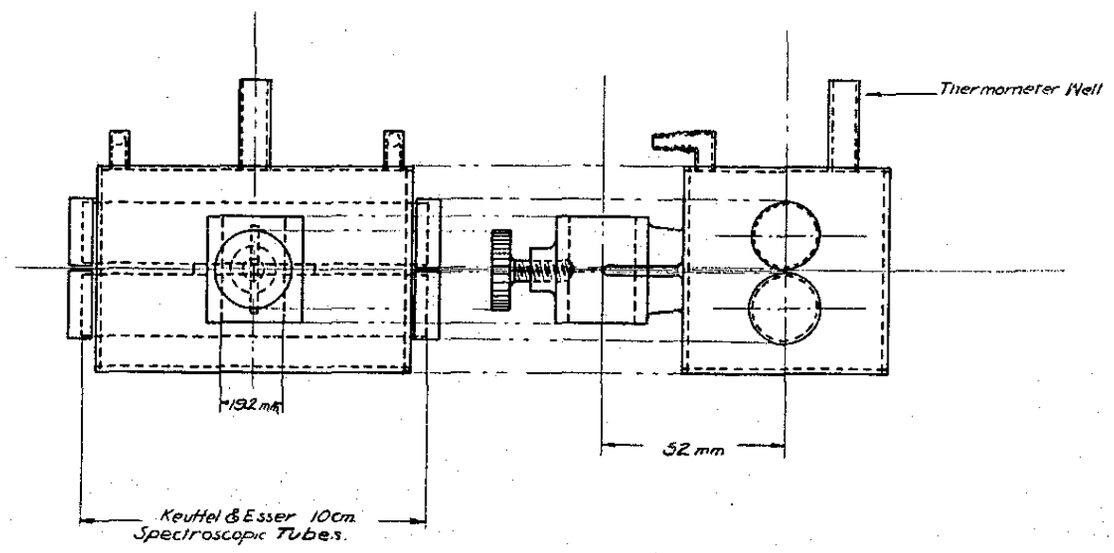


FIG. 1

maintenance of a uniform temperature of the solutions during the observation of the course of the reaction was necessary and, while approximately 20° was maintained, the heat from the apparatus gradually raised the temperature of the reacting vessels and good series of constants were difficult to obtain. As soon as it was found that the temperature coefficient of the reaction was considerable, a special casing for the spectroscopic tubes was devised, whereby they were surrounded by a stream of water fed from a large supply, thermostatically controlled at 20°. See Fig. 1.

All measuring flasks and pipettes were standardized by the U. S. Bureau of Standards.

b. The manipulation. The phenol solutions were made from a carefully purified sample of phenol. It was constant boiling and colorless. Liter quantities of a number of concentrations varying from 10^{-2} to 10^{-5} molar were made by dissolving in water.

The 2,6-dibromoquinonechloroimide was made as described in the third paper of this series and approximately concentrated solutions were made by shaking with water at 20° and filtering until clear. The water employed was practically ammonia free and no solutions over five hours old were employed.

The solutions were standardized by the spectrophotometric method of measuring the indophenol formation as described in the third paper of this series.

The buffering solutions employed were borate solutions of the Clark and Lubs series, and for the most accurate work were standardized electrometrically at the dilutions employed.

Portions of 5 cc of the various phenol solutions were run into a 50 cc measuring flask and then about 40 cc of the desired buffering solutions added. A measured volume, usually 1 to 2 cc, of the 2,6-dibromoquinonechloroimide solution was added, and the flask filled to the mark with the buffer. The spectroscope tube was filled with this solution, put in place in the spectrophotometer, and readings of the transmittancy taken at intervals of time measured by a stop watch. All readings were taken at $610_{m\mu}$, the peak of the absorption band for this indophenol. See third paper of this series.

The dissociation constant of 2, 6-dibromobenzenoneindophenol (pKa = 5.7) is such that at the pH values used experimentally there was complete dissociation and, therefore, full color. See Cohen, Gibbs and Clark (1924).

c. The calculations. The concentration of the sodium phenolate was calculated from the Ka value for phenol at 18° of 1.3×10^{-10}. J. Walker (1900.) The percentages of sodium phenolate in the various buffer solutions employed are given in Table I. Many of the buffered solutions enumerated were employed only in the preliminary work, the data for which is not recorded here since the determinations of the pH of the buffers was not considered sufficiently accurate.

TABLE I

Per cent of phenolate in various buffered phenol solutions

$$pH = \log \frac{1}{Ka} + \log \frac{salt}{acid}$$

Ka for phenol $= 1.3 \times 10^{-10}$ at 18°.

$pK_a = 9.89$

$$pH = 9.89 + \log \frac{\alpha}{1-\alpha}$$

pH	$\frac{acid}{salt}$	Per cent Na salt $\alpha \times 100$	pH	$\frac{acid}{salt}$	Per cent Na salt $\alpha \times 100$
8.4	30.90	3.14	9.28	4.074	19.71
8.5	24.55	3.91	9.3	3.89	20.45
8.6	19.50	4.88	9.4	3.09	24.45
8.733	14.35	6.51	9.5	2.46	28.90
8.884	10.14	8.92	9.528	2.301	30.29
9.0	7.76	11.42	9.6	1.95	33.90
9.129	5.768	14.77	9.917	0.9376	51.62
9.2	4.90	16.95	10.0	0.78	56.18

The amount of indophenol formed at any given time was found from the reading of the per cent transmittancy of the solution in the spectrophotometer, the value $-\log T = 1$ being that of an indophenol solution of a concentration of 5×10^{-6}. See third paper of this series.

The reaction velocity constant, "k", was calculated from the equation of a reaction of the first order

$$9. \qquad k = \frac{2.3026}{tb\alpha} \log \frac{a}{a-x}$$

where t = time in minutes, b = molar concentration of phenol, α = phenolate at the pH of the experiment, a = molar concentration of the 2, 6-dibromoquinonechloroimide, and x = amount of phenol or sodium phenolate, or 2, 6-dibromoquinonechloroimide reacting in time, "t", which is also equivalent to the amount of indophenol formed.

In two cases (see Tables XIII and XVIII) where the concentrations of the phenol and of the imide were nearly equal the velocity constant was also calculated from equation

$$7. \qquad k_2 = \frac{2.3026}{t\alpha(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

for a reaction of the second order. The agreement in the constants obtained in the various experiments indicate that the above described conceptions are correct.

d. Results. The final series of the reaction velocity experiments are recorded in Tables II-XXV inclusive.

The conditions of the 24 experiments and the velocity constants obtained are summarized in Table XXVI.

TABLE II

Reaction velocity of indophenol formation

a = 2,6-dibromoquinonechloroimide 3.24×10^{-6} molar
b = total phenol 10^{-3} molar
Buffer solution = pH 8.733
t = time in minutes
T = transmittancy x = indophenol formed in "t"
Ratios: $\frac{a}{\text{phenol}} = \frac{1}{309}$; $\frac{a}{\text{Na phenolate}} = \frac{1}{20}$

t	T	$-\log T$	x times 10^6	a−x times 10^{-6}	k
1	0.70	0.155	0.78	2.46	4.23×10^3
3	.44	.356	1.78	1.46	4.08
4	.37	.432	2.16	1.08	4.24
5	.31	.509	2.55	.69	4.75
6	.28	.553	2.77	.47	4.94
8	.26	.585	2.93	.31	4.51
11	.24	.620	3.10	.14	4.39
17	.225	.648	3.24	0.00	———
				Average	4.45×10^3

TABLE III

Reaction velocity of indophenol formation

a = 2,6-dibromoquinonechloroimide 3.24×10^{-6} molar
b = total phenol = 10^{-4} molar
Buffer solution = pH 8.733
t = time in minutes
T = transmittancy x = indophenol formed in "t"

Ratios: $\frac{a}{\text{phenol}} = \frac{1}{30.9}$; $\frac{a}{\text{Na phenolate}} = \frac{1}{2}$

t	T	−logT	x times 10^6	a−x times 10^{-6}	k
1	0.88	0.055	0.275	2.965	13.7×10^3
2	.80	.097	.485	2.755	12.2
3	.74	.131	.655	2.585	11.5
6	.55	.260	1.300	1.940	13.1
9	.41	.387	1.935	1.305	15.5
12	.37	.432	2.160	1.080	14.1
15	.34	.469	2.345	0.895	13.2
				Average	13.3×10^3

TABLE IV

Reaction velocity of indophenol formation

a = 2,6-dibromoquinonechloroimide 6.48×10^{-6} molar
b = Total phenol = 10^{-4} molar
Buffer solution = pH 8.733
t = time in minutes
T = transmittancy x = indophenol formed in "t"

Ratios: $\frac{a}{\text{phenol}} = \frac{1}{15.4}$; $\frac{a}{\text{Na phenolate}} = \frac{1}{1}$

t	T	−log T	x times 10^6	a−x times 10^{-6}	k
2	0.63	0.201	1.005	5.475	12.9×10^3
3	.50	.301	1.505	4.975	13.5
4	.44	.357	1.785	4.695	13.2
5	.35	.456	2.280	4.200	13.3
6	.29	.538	2.690	3.790	13.7
8	.22	.658	3.290	3.190	13.6
10	.18	.745	3.725	2.755	13.1
				Average	13.3×10^3

TABLE V

Reaction velocity of indophenol formation

a = 2,6-dibromoquinonechloroimide = 3.24×10^{-6} molar

b = Total phenol = 10^{-5} molar

Buffer solution = pH 8.733

t = time in minutes

T = transmittancy x = indophenol formed in "t"

Ratios: $\frac{a}{\text{phenol}} = \frac{1}{3.09}$; $\frac{a}{\text{Na phenolate}} = \frac{1}{0.2}$

t	T	−log T	x times 10^6	a−x times 10^6	k
3	0.95	0.022	0.110	3.130	17.7×10^3
5	.90	.046	.230	3.010	22.5
8	.85	.071	.355	2.885	22.2
13	.80	.097	.485	2.755	24.1
18	.74	.131	.655	2.585	19.2
22	.68	.168	.840	2.400	21.0
28	.65	.187	.935	2.305	18.7
				Average	20.7×10^3

TABLE VI

Reaction velocity of indophenol formation

a = 2,6-dibromoquinonechloroimide = 3.73×10^{-6} molar

b = Total phenol = 10^{-3} molar

Buffer solution = pH 9.129

t = time in minutes

T = transmittancy x = indophenol formed in "t"

Ratios: $\frac{a}{\text{phenol}} = \frac{1}{270}$; $\frac{a}{\text{Na phenolate}} = \frac{1}{40}$

t	T	−log T	x times 10^6	a−x times 10^6	k
1	0.38	0.420	2.100	1.630	5.61×10^3
2	.26	.585	2.925	.805	5.17
3	.20	.699	3.495	.235	6.24
4	.198	.703	3.515	.215	4.82
				Average	5.46×10^3

TABLE VII

Reaction velocity of indophenol formation

a = 2,6-dibromoquinonechloroimide = 5.23×10^{-6} molar

b = Total phenol = 10^{-3} molar

Buffer solution = pH 9.129

t = time in minutes

T = transmittancy x = indophenol formed in "t"

Ratios: $\frac{a}{\text{phenol}} = \frac{1}{191}$; $\frac{a}{\text{Na phenolate}} = \frac{1}{28}$

t	T	−log T	x times 10^5	a−x times 10^5	k
1	0.260	0.585	2.925	2.305	5.55×10^3
2	.125	.903	4.515	.715	6.73
3	.090	1.046	5.230	.000	———
				Average	6.14×10^3

TABLE VIII

Reaction velocity of indophenol formation

a = 2,6-dibromoquinonechloroimide = 3.73×10^{-6} molar

b = Total phenol = 10^{-4} molar

Buffer solution = pH 9.129

t = time in minutes

T = transmittancy x = indophenol formed in "t"

Ratios: $\frac{a}{\text{phenol}} = \frac{1}{27}$; $\frac{a}{\text{Na phenolate}} = \frac{1}{4}$

t	T	−log T	x times 10^5	a−x times 10^6	k
2	0.54	0.278	1.39	2.34	15.78×10^3
3	.44	.356	1.78	1.95	14.64
4	.38	.420	2.10	1.63	14.01
5	.34	.468	2.34	1.39	16.80
				Average	15.31×10^3

Note: Comparison tube contained buffer plus the same amount of 2,6-dibromoquinonechloroimide.

TABLE IX

Reaction velocity of indophenol formation

a = 2,6-dibromoquinonechloroimide = 5.23×10^{-6} molar

b = Total phenol = 10^{-4} molar

Buffer Solution = pH 9.129

t = time in minutes

T = transmittancy x = indophenol formed in "t"

Ratios: $\frac{a}{\text{phenol}} = \frac{1}{19}; \frac{a}{\text{Na phenolate}} = \frac{1}{2.9}$

t	T	−log T	x times 10^6	a−x times 10^6	k
2	0.46	0.337	1.67	3.56	13.05×10^3
3	.32	.495	2.48	2.75	14.51
4	.24	.620	3.10	2.13	15.20
5	.185	.733	3.67	1.56	16.38
6	.16	.796	3.98	1.25	16.15
7	.15	.824	4.12	1.11	14.99
				Average	15.05×10^3

TABLE X

Reaction velocity of indophenol formation

a = 2,6-dibromoquinonechloroimide = 5.23×10^{-6} molar

b = Total phenol = 10^{-5} molar

Buffer solution = pH 9.129

t = time in minutes

T = transmittancy x = indophenol formed in "t"

Ratios: $\frac{a}{\text{phenol}} = \frac{1}{1.9}; \frac{a}{\text{Na phenolate}} = \frac{1}{0.29}$

t	T	−log T	x times 10^6	a−x times 10^6	k
4.5	0.72	0.143	0.72	4.51	22.27×10^3
5	.70	.155	.78	4.45	21.85
6	.66	.180	.90	4.33	21.30
7	.61	.215	1.08	4.15	22.39
8	.56	.252	1.26	3.97	23.32
9	.51	.292	1.46	3.77	24.63
				Average	22.63×10^3

TABLE XI

Reaction velocity of indophenol formation

a = 2,6-dibromoquinonechloroimide = 3.73×10^{-6} molar
b = Total phenol = 10^{-5} molar
Buffer solution = pH 9.129
t = time in minutes
T = Transmittancy x = indophenol formed in "t"

Ratios: $\frac{a}{\text{phenol}} = \frac{1}{2.7}$; $\frac{a}{\text{Na phenolate}} = \frac{1}{0.4}$

t	T	−log T	x times 10^6	a−x times 10^6	k
3	0.86	0.066	0.33	3.40	20.89×10^3
4	.81	.092	.46	3.27	22.29
6	.74	.131	.66	3.07	21.38
11	.61	.215	1.08	2.65	21.05
				Average	21.40×10^3

TABLE XII

Reaction velocity of indophenol formation

a = 2,6-dibromoquinonechloroimide = 7.46×10^{-6} molar
b = Total phenol = 10^{-5} molar
Buffer solution = pH 9.129
t = time in minutes
T = transmittancy x = indophenol formed in "t"

Ratios: $\frac{a}{\text{phenol}} = \frac{1}{1.34}$; $\frac{a}{\text{Na phenolate}} = \frac{1}{0.2}$

t	T	−log T	x times 10^6	a−x times 10^6	k
2	0.78	0.108	0.54	6.92	$(25.41) \times 10^3$
3	.74	.131	.66	6.80	20.89
4	.68	.168	.84	6.62	20.18
6	.53	.276	1.38	6.08	23.07
8	.46	.337	1.69	5.77	21.73
10	.42	.377	1.89	5.57	19.77
				Average	21.13×10^3

TABLE XIII

Reaction velocity of indophenol formation.

a = phenol = 10^{-5} molar

b = 2,6-dibromoquinonechloroimide = 7.46×10^{-6} molar

Buffer solution = pH 9.129

t = time in minutes

T = transmittancy x = indophenol formation in "t"

Ratios: $\frac{b}{\text{phenol}} = \frac{1}{1.34}; \frac{b}{\text{Na phenolate}} = \frac{1}{0.2}$

calculated according to formula $k_2 = \frac{2.3026}{t\alpha(a-b),} \log \frac{b(a-x)}{a(b-x)}$ from same data as table XII.

t	T	−log T	x times 10^6	b−x times 10^6	a−x times 10^6	k_2
2	0.78	0.108	0.54	6.92	9.46	$(26.10) \times 10$
3	.74	.131	.62	6.84	9.38	20.05
4	.68	.168	.84	6.62	9.16	21.04
6	.53	.276	1.38	6.08	8.62	24.86
8	.46	.337	1.69	5.77	8.31	23.87
10	.42	.377	1.89	5.57	8.11	21.99
					Average	22.36×10^3

TABLE XIV

Reaction velocity of indophenol formation

a = 2,6-dibromoquinonechloroimide = 3.73×10^{-6} molar

b = Total phenol = 5×10^{-5} molar

Buffer solution = pH 9.129

t = time in minutes

T = transmittancy x = indophenol formed in "t"

Ratios: $\frac{a}{\text{phenol}} = \frac{1}{13.4}; \frac{a}{\text{Na phenolate}} = \frac{1}{2}$

t	T	−log T	x $\times 10^6$	a−x $\times 10^6$	k
2	0.69	0.161	0.81	2.92	16.95×10^3
3	.59	.229	1.30	2.43	19.34
4	.50	.301	1.52	2.21	17.71
5	.42	.377	1.89	1.84	19.14
8	.36	.444	2.22	1.51	15.31
				Average	17.69×10^3

TABLE XV

Reaction velocity of indophenol formation

a = 2,6-dibromoquinonechloroimide = 4×10^{-6} molar
b = Total phenol = 10^{-3} molar
Buffer solution = pH 9.528
t = time in minutes
T = transmittancy x = indophenol formed in "t"

Ratios: $\frac{a}{\text{phenol}} = \frac{1}{250}; \frac{a}{\text{Na phenolate}} = \frac{1}{76}$

t	T	−log T	$\frac{x}{\times 10^6}$	$\frac{a-x}{\times 10^6}$	k
1	0.28	0.553	2.77	1.23	3.92×10^3
2	.19	.721	3.62	.38	3.88
3	.17	.770	3.85	.15	3.61
				Average	3.80×10^3

TABLE XVI

Reaction velocity of indophenol formation

a = 2,6-dibromoquinonechloroimide = 4×10^{-6} molar
b = Total phenol = 10^{-4} molar
Buffer solution = pH 9.528
t = time in minutes
T = transmittancy x = indophenol formation in "t"

Ratios: $\frac{a}{\text{phenol}} = \frac{1}{25}; \frac{a}{\text{Na phenolate}} = \frac{1}{7.6}$

t	T	−log T	$\frac{x}{\times 10^6}$	$\frac{a-x}{\times 10^6}$	k
2	0.32	0.495	2.475	1.525	15.92×10^3
3	.25	.602	3.010	.990	15.38
4	.214	.670	3.350	.650	15.00
5	.196	.708	3.540	.460	14.28
				Average	15.15×10^3

TABLE XVII

Reaction velocity of indophenol formation
a = 2,6-dibromoquinonechloroimide = 4×10^{-6} molar
b = Total phenol = 10^{-5} molar
Buffer solution = pH 9.528
t = time in minutes
T = transmittancy x = indophenol formed in "t"

Ratios: $\frac{a}{\text{phenol}} = \frac{1}{2.5}$; $\frac{a}{\text{Na phenolate}} = \frac{1}{0.76}$

t	T	−log T	x times 10^6	a−x times 10^6	k
4	0.72	0.143	0.72	3.28	16.38×10^3
5	.65	.187	.94	3.06	17.70
6	.61	.215	1.08	2.92	17.30
7	.56	.252	1.26	2.74	17.82
8	.53	.276	1.38	2.62	17.50
9	.52	.284	1.42	2.58	16.07
				Average	17.11×10^3

TABLE XVIII

Reaction velocity of indophenol formation.
a = phenol = 10^{-5} molar
b = 2,6-dibromoquinonechloroimide = 4×10^{-6} molar
Buffer solution = pH 9.528
t = time in minutes
T = transmittancy x = indophenol formed in "t"

Ratios: $\frac{b}{\text{phenol}} = \frac{1}{2.5}$; $\frac{b}{\text{Na phenolate}} = \frac{1}{0.76}$

k_2 calculated according to formal $k_2 = \frac{2.3026}{t\alpha(a-b)} \log \frac{b(a-x)}{a(b-x)}$ from same data as table 17.

t	T	−log T	x times 10^6	b−x times 10^6	a−x times 10^6	k_2
4	0.72	0.143	0.72	3.28	9.28	(16.98) 10 $\times^3$
5	.65	.187	.94	3.06	9.06	18.60
6	.61	.215	1.08	2.92	8.92	18.36
7	.56	.252	1.26	2.74	8.74	19.12
8	.53	.276	1.38	2.62	8.62	18.87
9	.52	.284	1.42	2.58	8.58	17.43
12	.50	.301	1.51	2.49	8.49	(14.21)
					Average	18.47×10^3

TABLE XIX

Reaction velocity of indophenol formation

a = 2,6-dibromoquinonechloroimide = 3.73×10^{-6} molar

b = Total phenol = 10^{-3} molar

Buffer solution = pH 9.917

t = time in minutes

T = transmittancy x = indophenol formed in "t"

Ratios: $\frac{a}{\text{phenol}} = \frac{1}{268}$; $\frac{a}{\text{Na phenolate}} = \frac{1}{138}$

t	T	−log T	x times 10^5	a−x times 10^6	k
2	0.24	0.620	3.10	0.63	1.68×10^3
3	.225	.648	3.24	.49	1.31
5	.205	.688	3.44	.29	1.00
				Average	1.33×10^3

TABLE XX

Reaction velocity of indophenol formation

a = 2,6-dibromoquinonechloroimide = 3.2×10^{-6} molar

b = Total phenol = 10^{-3} molar

Buffer solution = pH 9.917

t = time in minutes

T = Transmittancy x = indophenol formed in "t"

Ratios: $\frac{a}{\text{phenol}} = \frac{1}{313}$; $\frac{a}{\text{Na phenolate}} = \frac{1}{161}$

t	T	−log T	x times 10^6	a−x times 10^5	k
2	0.38	0.420	2.10	1.10	1.04×10^3
3	.25	.602	3.01	.19	1.82
4	.24	.620	3.10	.10	1.73
				Average	1.53×10^3

TABLE XXI

Reaction velocity of indophenol formation

a = 2,6-dibromoquinonechloroimide = 3.73×10^{-6} molar

b = Total phenol = 10^{-4} molar

Buffer solution = pH 9.917

t = time in minutes

T = Transmittancy x = indophenol formed in "t"

Ratios: $\frac{a}{\text{phenol}} = \frac{1}{27}; \frac{a}{\text{Na phenolate}} = \frac{1}{13.8}$

t	T	−log T	x times 10^6	a−x times 10^6	k
1.5	0.41	0.387	1.935	1.795	9.45×10^3
2	.33	.482	2.410	1.320	10.04
3	.30	.523	2.615	1.115	7.80
				Average	9.10×10^3

TABLE XXII

Reaction velocity of indophenol formation

a = 2,6-dibromoquinonechloroimide = 3.20×10^{-6} molar

b = Total phenol = 10^{-4} molar

Buffer solution = pH 9.917

t = time in minutes

T = transmittancy x = indophenol formed in "t"

Ratios: $\frac{a}{\text{phenol}} = \frac{1}{31}; \frac{a}{\text{Na phenolate}} = \frac{1}{16}$

t	T	−log T	x times 10^6	a−x times 10^6	k
1	0.48	0.319	1.60	1.60	13.43×10^3
2	.32	.495	2.48	.72	14.45
3	.29	.538	2.69	.51	11.86
				Average	13.25×10^3

TABLE XXIII

Reaction velocity of indophenol formation

a = 2,6-dibromoquinonechloroimide = 3.20×10^{-6} molar

b = Total phenol = 5×10^{-5} molar

Buffer solution = pH 9.917

t = time in minutes

T = transmittancy x = phenol formed in "t"

Ratios: $\frac{a}{\text{phenol}} = \frac{1}{16}; \frac{a}{\text{Na phenolate}} = \frac{1}{8}$

t	T	−log T	x times 10^6	a−x times 10^6	k
1	0.61	0.215	1.08	2.12	15.97×10^3
2	.46	.337	1.69	1.51	14.51
3	.37	.432	2.16	1.04	14.52
				Average	15.00×10^3

TABLE XXIV

Reaction velocity of indophenol formation

a = 2,6-dibromoquinonechloroimide = 3.73×10^{-6} molar

b = Total phenol = 5×10^{-5}

Buffer solution = pH 9.917

t = time in minutes

T = transmittancy x = indophenol formed in "t"

Ratios: $\frac{a}{\text{phenol}} = \frac{1}{13}$; $\frac{a}{\text{Na phenolate}} = \frac{1}{7}$

t	T	$-\log T$	x times 10^6	a−x times 10^6	k
1.5	0.54	0.268	1.34	2.39	11.45×10^3
2	.44	.356	1.78	1.95	12.57
3	.38	.420	2.10	1.63	10.69
4	.36	.444	2.22	1.51	8.76
				Average	10.87×10^3

TABLE XXV

Reaction velocity of indophenol formation

a = 2,6-dibromoquinonechloroimide = 3.73×10^{-6} molar

b = Total phenol = 10^{-5} molar

Buffer solution = pH 9.917

t = time in minutes

T = transmittancy x = indophenol formed in "t"

Ratios: $\frac{a}{\text{phenol}} = \frac{1}{2.7}$; $\frac{a}{\text{Na phenolate}} = \frac{1}{1.38}$

t	T	$-\log T$	x times 10^6	a−x times 10^6	k
2	0.72	0.143	0.72	3.01	20.29×10^3
3	.64	.194	.97	2.76	19.45
4	.56	.252	1.26	2.47	19.96
6	.52	.284	1.42	2.31	(15.50)
				Average	19.90×10^3

TABLE XXVI

Summary of reaction velocity data from Tables II-XXV inclusive

Table No.	pH	Molar concentrations: Phenol	Molar concentrations: 2, 6-dibrom-quinone-chloroimide	Phenolate	Ratios of the concentration of 2,6-dibromoquinone chloroimide to: Phenol	Ratios of the concentration of 2,6-dibromoquinone chloroimide to: Phenolate	k
2	8.733	10^{-3}	3.24×10^{-6}	6.51×10^{-5}	1 : 309	1 : 20	$(4.45) \times 10^{3}$
3	8.733	10^{-4}	3.24×10^{-6}	6.51×10^{-6}	1 : 30.9	1 : 2	13.30
4	8.733	10^{-4}	6.48×10^{-6}	6.51×10^{-6}	1 : 15.4	1 : 1	13.30
5	8.733	10^{-5}	3.24×10^{-6}	6.51×10^{-7}	1 : 3.09	1 : 0.2	20.70
6	9.129	10^{-3}	3.73×10^{-6}	1.477×10^{-4}	1 : 270	1 : 40	(5.46
7	9.129	10^{-3}	5.23×10^{-6}	1.477×10^{-4}	1 : 191	1 : 28	(6.14)
8	9.129	10^{-4}	3.73×10^{-6}	1.477×10^{-5}	1 : 27	1 : 4	15.31
9	9.129	10^{-4}	5.23×10^{-6}	1.477×10^{-5}	1 : 19	1 : 2.9	15.05
10	9.129	10^{-5}	5.23×10^{-6}	1.477×10^{-6}	1 : 1.9	1 : 0.29	22.63
11	9.129	10^{-5}	3.73×10^{-6}	1.477×10^{-6}	1 : 2.7	1 : 0.4	21.40
12	9.129	10^{-5}	7.46×10^{-6}	1.477×10^{-6}	1 : 1.34	1 : 0.2	21.13
13	9.129	10^{-5}	7.46×10^{-6}	1.477×10^{-6}	1 : 1.34	1 : 0.2	22.36
14	9.129	5×10^{-5}	3.73×10^{-6}	7.385×10^{-6}	1 : 13.4	1 : 2	17.69
15	9.528	10^{-3}	4×10^{-6}	3.03×10^{-4}	1 : 250	1 : 76	(3.80)
16	9.528	10^{-4}	4×10^{-6}	3.03×10^{-5}	1 : 25	1 : 7.6	15.15
17	9.528	10^{-5}	4×10^{-6}	3.03×10^{-6}	1 : 2.5	1 : 0.76	17.11
18	9.528	10^{-5}	4×10^{-6}	3.03×10^{-6}	1 : 2.5	1 : 0.76	18.47
19	9.917	10^{-3}	3.73×10^{-6}	5.162×10^{-4}	1 : 268	1 : 138	(1.33)
20	9.917	10^{-3}	3.2×10^{-6}	5.162×10^{-4}	1 : 313	1 : 161	(1.53)
21	9.917	10^{-4}	3.73×10^{-6}	5.162×10^{-5}	1 : 27	1 : 13.8	9.10
22	9.917	10^{-4}	3.20×10^{-6}	5.162×10^{-5}	1 : 31	1 : 16	13.25
23	9.917	5×10^{-5}	3.20×10^{-6}	2.581×10^{-6}	1 : 16	1 : 8	15.00
24	9.917	5×10^{-5}	3.73×10^{-6}	2.581×10^{-6}	1 : 13	1 : 7	10.87
25	9.917	10^{-5}	3.73×10^{-6}	5.162×10^{-6}	1 : 2.7	1 : 1.38	19.90
						Average	16.76×10^{3}

Discussion

It is to be noted from a study of Table XXVI that experiments are recorded and reaction velocities measured in solutions when the phenol concentration varied from 10^{-3} to 5×10^{-5} molar, the sodium phenolate varied from 5.162×10^{-4} to 6.51×10^{-7} molar and the 2,6-dibromoquinonechloroimide varied from 7.46×10^{-6} to 3.20×10^{-6} molar. The ratios of these substances varied in the various experiments recorded from the highest values of

313 parts of phenol to 1 part of 2,6-dibromoquinonechloroimide
161 parts of sodium phenolate to 1 part of 2,6-dibromoquinonechloroimide
to the lowest values of
1.34 parts of phenol to 1 part 2,6-dibromoquinonechloroimide
0.2 parts of sodium phenolate to 1 part 2,6-dibromoquinonechloroimide

Eighteen of the values give fairly satisfactory agreement in the velocity constant, "k". The average of these 18 values is 1.68×10^{4}.

In these 18 experiments the ratios of the phenol and sodium phenolate to the 2,6-dibromoquinonechloroimide varied from the highest value of

31 parts of phenol to 1 part of imide
16 parts of sodium phenolate to 1 part of imide
to the lowest value of
1.34 parts of phenol to 1 part of imide
0.2 part of sodium phenolate to 1 part of imide.

When the concentration of sodium phenolate is greater than 16 times that of the imide the reaction is so rapid that the measurements are very uncertain. The constant seems to fall off rapidly under these conditions. It, therefore, seems reasonable to exclude the six values for "k" given in parentheses in Table XXVI, in obtaining the average value of 1.63×10^{4}.

The accuracy of this value is dependent upon many experimental factors which were controlled as carefully as possible and also, basically, upon the Ka value for phenol which was determined by J. Walker in 1900 to be 1.3×10^{-10} at 18°.

Stenström and Goldsmith (1926) have recently determined the dissociation constant of phenol by measuring the ultraviolet absorption at wave length 2825Å at pH values varying from 4.5 to 13. The desired values of pH were obtained by the addition of sodium hydroxide solution and were determined colorimetrically. The temperature during the exposures varied between 18° and 24°. They reported two values 1.38×10^{-10} and 1.21×10^{-10} the average of which is 1.295×10^{-10}. This work does not afford any grounds for the correction of the values of Walker employed in my work. The actual activity coefficient of the phenolate ion in the buffers employed in this experimental work are not known and it is interesting to note that a change of Ka from 1.3×10^{-10} to 2.3×10^{-10} may, in some cases, reduce the reaction velocity constant by so much as 50 per cent.

It is, therefore, believed that an error arising from this source may be greater than that produced by any factor entering into my experiments. Since it has been my purpose to elucidate the underlying mechanism of the

reactions involved in the indophenol formation, rather than determine a reaction velocity constant with great accuracy, for practical purposes it has not seemed necessary to redetermine the Ka value of phenol.

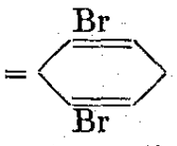
It has been found that 2,6-dibromoquinonechloroimide decomposes in alkaline solution giving rise to an increased coloration. This is visible at 610mμ, the wave length of the peak of the absorption band of the indophenol, and therefore, any of the imide which decomposes and escapes reaction with the phenol in the indophenol reaction will introduce an error into the readings. However, the amount of this decomposition during the indophenol reaction is very small, much less than the amount of decomposition in the alkaline buffers when phenol is absent. Any correction to be introduced for this cause seems to be negligible, and overshadowed by other errors of experimentation.

A few experiments were performed employing an equal concentration of the imide and the same buffer solution in the comparison tube as employed in the reaction vessel. That is to say that the reaction tube and the comparison tube were equal in every respect, except that the former contained phenol while in the latter it was absent.

The reaction velocity experiment recorded in Table VIII was performed in this manner. This, and other similar experiments, showed that the error from the decomposition of the 2,6-dibromoquinonechloroimide was very slight and indicated that water, or buffer solution, in the comparison tube was to be preferred.

A study of the decomposition of 2,6-dibromoquinonechloroimide in various buffers was undertaken.

The Reaction of 2, 6-dibromoquinonechloroimide in Alkaline Buffers

The coloration of 2,6-dibromoquinonechloroimide, O=  =NCl, in alkaline solutions can be followed by means of the spectrophotometer. Since the rate of reaction is accelerated by light, the readings were made as quickly as possible with the light passing through the solution for the shortest interval of time.

The reactions give a light red solution which has very little absorption in the red. The greatest absorption is the blue. The absorption of the solution was investigated at various concentrations in the visible region of the spectrum, at which range it shows no particular evidence of the development of bands but only a gradual increase in absorption from the red to the blue. See Fig. 2.

The rate of change was first followed by reading the absorption at 610mμ for the reason that this wave length is the peak of the absorption band of the corresponding indophenol and it was, therefore, hoped to obtain results useful in the correction of the indophenol reaction velocity. The rate of change was also followed by measurements made at 520mμ, a region nearer the maximum absorption. The 2,6-dibromoquinonechloroimide solutions employed were standardized with phenol by measurements of the indophenol

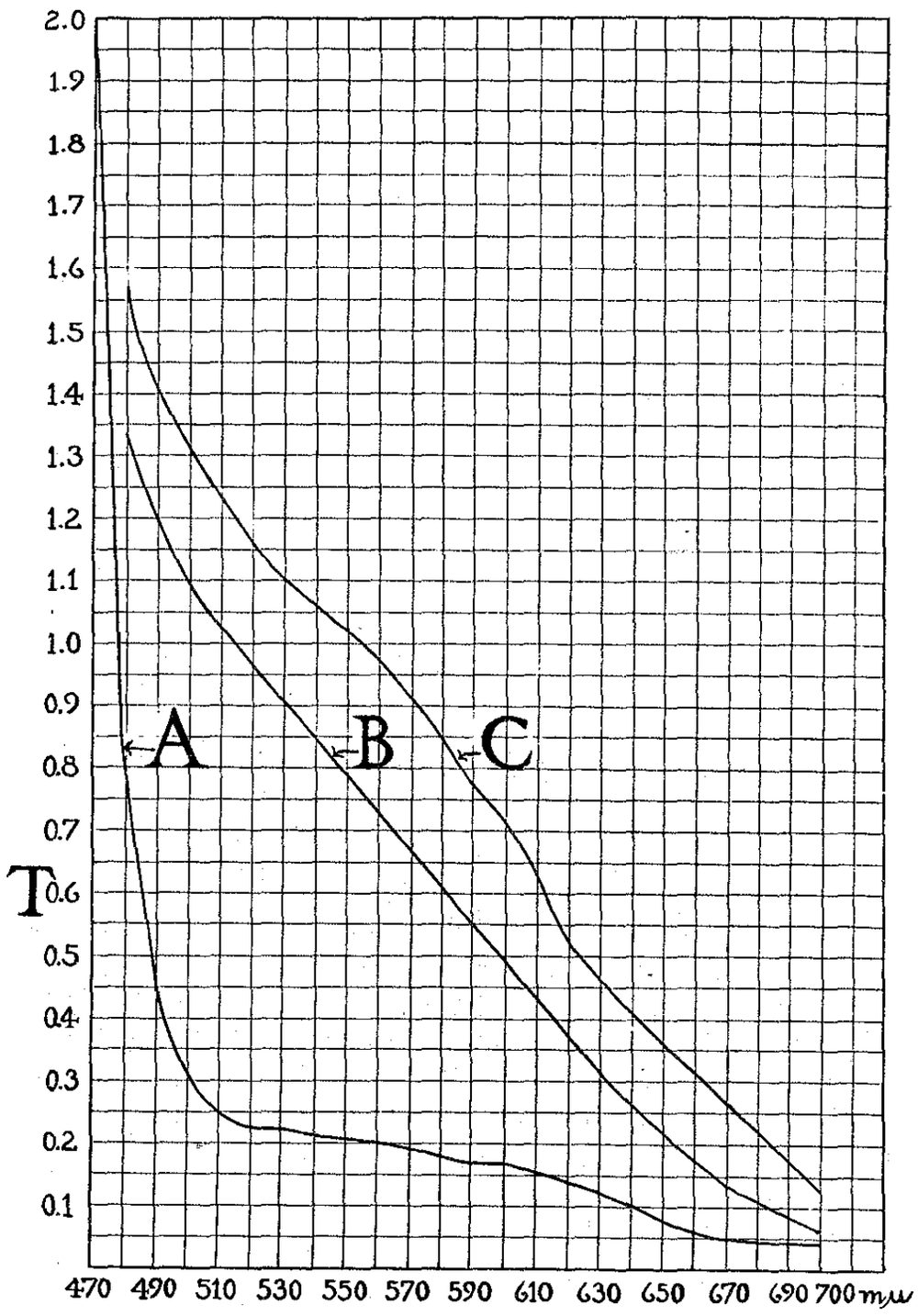


FIG. 2

A. Absorption curve of 2, 6-dibromoquinoneoxime 4.25×10^{-4} molar. Only slight deviations occur in this curve from pH 8 to pH 10.

B. Absorption curve of an alkaline solution of 2, 6-dibromoquinonechloroimide after the reaction had proceeded for 8 minutes at pH 9.13. 1.37×10^{-5} molar. The position of this curve is raised by prolonged action or increase in pH.

C. Same as "B" except pH 9.53.

All values of T read in 10 cm tubes. Ordinates $= -\log T$.

formation as previously described. They were then measured into alkaline buffer solutions and the color formation observed spectrophotometrically. Since neither the pure color compound nor its absorption spectrum are known, the maximum absorption obtained at a standard wave length, 610 and 520mμ, was taken as complete transformation of the imide and the intermediate values for "x", the amount of imide transformed in time "t" calculated therefrom.

The rate of change was found to vary greatly with the pH and measurements were, therefore, made at values varying from pH 8.5 to 10.0. Constant values were obtained in each experiment when calculated according to a reaction of the first order. When these values are divided by the concentration of the hydroxyl ion all of the experiments at varying pH values are brought into agreement, the average of seven experiments at pH 8.5, 9.0, 9.13, 9.5, 9.53 and 10 being 6.13×10^3.

It is therefore evident that the reaction under consideration is pseudo monomolecular and the equation

$$10. \qquad k = \frac{1}{tc} \ln \frac{a}{a-x}$$

where t = time in minutes, c = hydroxyl concentration of the buffers, a = 2,6-dibromoquinonechloroimide and x = amount transformed in "t", is a true representation of the conditions.

The hydroxyl ion concentration has been calculated from the pH value by means of the expression

$$11. \qquad pH = \log \frac{1}{H^+}$$

employing the value of 14 for hk_w. Since the dilution and other experimental factors not accurately determined may effect this value it seemed trivial to correct Kw for temperature.

The seven reaction velocity experiments are recorded in Tables XXVII-XXXIII, inclusive, and a summary of the data is given in Table XXXIV.

The values of k_1 and k_2 recorded in these seven tables are obtained from the formulae

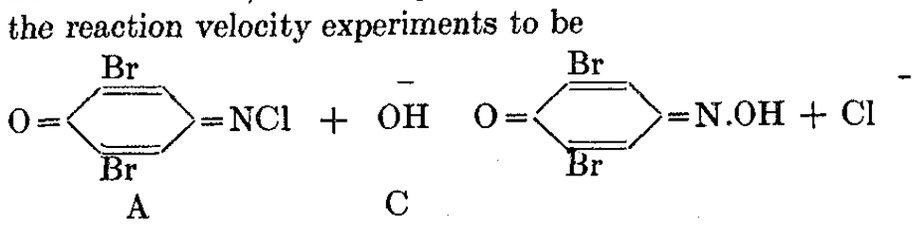
$$12. \qquad k_1 = \frac{2.3026}{t} \log \frac{a}{a-x}$$

$$13. \qquad k_2 = \frac{2.3026}{tc} \log \frac{a}{a-x}$$

While the constants obtained leave much to be desired in agreement and accuracy, the effect of pH is definitely shown and magnitude of the constant is indicated. The tendency of the value of k_1 and k_2 to increase with time in some of the experiments is attributed to the accelerating effect of light, since in these experiments the irradiation was excessive due to the fact that readings were taken at several wave lengths.

2, 6-Dibromoquinoneoxime (2, 6-dibromonitrosophenol)

The reaction between 2,6-dibromoquinonechloroimide and alkalies is indicated by the reaction velocity experiments to be



A C

2,6-dibromoquinoneoxime being the principal reaction product.

In order to obtain some evidence upon the nature of the reaction, pure 2,6-dibromoquinoneoxime (nitrosophenol) was prepared by brominating p-nitrosophenol as described by O. Fischer and E. Hepp (1888).

A saturated aqueous solution at 20° of this preparation was found to be 8.5×10^{-4} molar as calculated from the determination of the nitrogen.

One hundred cc of solution gave 0.00119 g nitrogen. This solubility compares with 1.88×10^{-2} molar for the unbrominated derivative. (See second paper of this series.) The compound was found to vary in the color of its solutions from colorless at pH 3 to a yellow green in 0.2 N sodium hydroxide. The dissociation constant of this preparation, determined by the method of Salm (1906), is 4.6 in terms of pKa. This compares with 6.4 for the unbrominated compound. (See second paper of this series.) The solutions employed were: for the acid solution 1 cc of the saturated 2,6-dibromonitrosophenol solution plus 10 cc of buffer pH 3; for the alkaline solution 1 cc of 2,6-dibromonitrosophenol solution plus 10 cc of 0.2N sodium hydroxide. Superpositions of these were matched against 2 cc of solution plus 9 cc of buffer pH 4.6 and 11 cc of water.

The adsorption spectra of solutions of 2,6-dibromoquinoneoxime were measured in aqueous solution and at pH 8, 9 and 10, and very slight differences were observed under these conditions. Five cc of the saturated solution were mixed with 5 cc of the buffer solution.

The typical curve is plotted in Fig. 2. It is quite flat from 700mμ to 500mμ showing very little absorption in this region but rises rapidly showing almost complete absorption in the blue. There is some evidence of the formation of an incipient absorption band heading about 600mμ which seems to be the most evident at pH 8.5 although not very marked under any of the conditions employed.

2,6-Dibromoquinoneoxime is quite stable in aqueous solution. In a buffered solution at pH 8.5 no change in the absorption spectrum was noted on 24 hours standing at room temperature. This is in striking contrast to the unbrominated oxime.

Discussion

From the previously described data, it is considered proved that 2,6-dibromoquinonechloroimide reacts in alkaline solution, the velocity of the reaction showing it to be pseudo monomolecular the speed being determined by the concentration of the hydroxyl ion. The absorption curve of the resulting solution bears a sufficient similarity to that of 2,6-dibromoquinoneoxime,

see FIG. 2, to suggest that while the latter is not the only product it may be the first and most important stage of the reaction, other condensations later taking place to a more or less limited extent.

The possibility of correcting the reaction velocity constant for the indophenol formation from any data obtained from a study of the decomposition of 2,6-dibromoquinonechloroimide alone in alkaline solutions seems to be rather remote and perhaps immaterial. If the velocity constant for the complete decomposition of the 2,6-dibromoquinonechloroimide were employed it would reduce the velocity constant for the indophenol formation by only one-third. The decomposition of the 2,6-dibromoquinonechloroimide is evidentally practically negligible when phenol is present to unite with it and the indophenol reaction proceeds. This is shown by the excellent results that are obtained by the standardization of the imide solutions by the indophenol formation at various pH ranges when a great excess of phenol is present. When the reacting quantities of 2,6-dibromoquinonechloroimide and phenol are nearly equal in molarity another state of affairs exists, and under these conditions, there is no doubt but that the decomposition of the imide is a material factor and that the maximum indophenol formation, as measured either by the amount of phenol present or the amount of imide present, is never reached. This can be attributed to the reaction of the 2,6-dibromoquinonechloroimide with the alkali present.

It is, therefore, evident that to obtain good results in the quantitative determination of phenol a considerable excess of the 2,6-dibromoquinonechloroimide must be present and, vice versa, in standardizing 2,6-dibromoquinonechloroimide solutions a large excess of phenol must be present. In the latter case the maximum indophenol formation will take place before the amount of imide decomposed by the alkali becomes material.

Summary

The reaction between 2,6-dibromoquinonechloroimide and phenol, producing 2,6-dibromobenzenoneindophenol, has been quantitatively studied at various pH ranges in the alkaline region and the reaction velocity measured spectrophotometrically. This reaction has been found to take place in the alkaline region between 2,6-dibromoquinonechloroimide and the sodium phenolate and in buffered solutions with a large excess of phenol the reaction is pseudo monomolecular and is expressed by the equation

$$k = \frac{2.3026}{tb\alpha} \log \frac{a}{a-x}.$$

When the concentrations of the phenol and the imide are nearly equal, the same value for the constant is obtained by calculations according to a reaction of the second order

$$k_2 = \frac{2.3026}{t\alpha\,(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

The average value of k is 1.63×10^4 at 20°.

The production of this indophenol, giving a blue color in alkaline solutions, has been found to be a very delicate test for phenol and the reaction velocity has been measured at phenol concentrations below the limit of many of the heretofore known phenol tests.

The reaction has a considerable temperature coefficient and therefore the studies were carried on in specially constructed apparatus to maintain this factor constant.

2,6-Dibromoquinonechloroimide decomposes in alkaline solution and a study of the rate of this decomposition in various alkaline buffers shows that the reaction is pseudo monomolecular, the rate varying greatly with the hydroxyl ion concentration, and can be presented by the equation

$$k_2 = \frac{2.3026}{tc} \log \frac{a}{a-x}$$

in which t = time in minutes, c = $O\bar{H}$, a = 2,6-dibromoquinonechloroimide and x the amount reacting in time "t". The average of seven reaction velocity experiments indicates the value of k_2 to be 6.13×10^3.

It is indicated that 2,6-dibromoquinoneoxime is the primary product of the reaction but that other colored compounds are formed.

2,6-Dibromoquinoneoxime has been prepared and studied. The solubility in water at 20° is 8.5×10^{-4} molar, and the pKa value is 4.6.

The absorption spectra of 2,6-dibromoquinoneoxime, and of alkaline solutions of 2,6-dibromoquinonechloroimide are charted.

x

TABLE XXVII

Reaction velocity of 2,6-Dibromoquinonechloroimide in alkaline buffer solutions.

a = 2,6-dibromoquinonechloroimide = 1.8×10^{-5} molar

c = OH^- at pH 8.5

t = time in minutes; x = "a" transformed in "t"; T = transmittancy

The maximum absorption or final value of T = 0.31

Spectrophotometric readings at 610 mμ; 10 cm tubes

Temperature 20°

t	T	−log T	x times 10^5	a−x times 10^5	k_1	k_2
2	0.97	0.013	0.046	1.754	(0.013)	(4.1×10^3)
4	.91	.041	.145	1.655	.021	6.6
6	.86	.065	.230	1.570	.023	7.2
9	.815	.087	.308	1.492	.021	6.6
12	.78	.108	.382	1.418	.020	6.3
15	.75	.125	.443	1.357	.019	6.0
21	.68	.167	.590	1.210	(.017)	(5.3)
27	.66	.180	.637	1.163	———	———
				Average	0.021	6.5×10^3

It is shown that solutions of phenol and solutions of 2,6-dibromoquinonechloroimide can be accurately standardized by means of measurements of this indophenol formation.

The experimental results are recorded in 34 tables. Two figures and a bibliography are included.

Table XXVIII

Reaction velocity of 2,6-Dibromoquinonechloroimide in alkaline buffer solutions.

a = 2,6-dibromoquinonechloroimide = 1.8×10^{-5} molar
c = OH^- at pH 9.0
t = time in minutes; x = "a" transformed in "t"; T = transmittancy
The maximum absorption or final value of T = 0.31
Spectrophotometric readings at 610 mμ; 10 cm tubes
Temperature 20°

t	T	−log T	x times 10^5	a−x times 10^5	k_1	k_2
2	0.86	0.065	0.230	1.570	(0.0684)	$(6.8) \times 10^3$
4	.76	.119	.421	1.379	.0628	6.3
6	.70	.155	.548	1.252	.0605	6.1
9	.64	.194	.686	1.114	.0533	5.3
13	.55	.260	.916	0.884	.0547	5.5
				Average	0.0578	5.8×10^3

Table XXIX

Reaction velocity of 2,6-dibromoquinonechloroimide in alkaline buffer solutions.

a = 2,6-dibromoquinonechloroimide = 1.8×10^{-5} molar
c = OH^- at pH 9.5
t = time in minutes; x = "a" transformed in "t"; T = transmittancy
The maximum absorption or final value of T = 0.31
Spectrophotometric readings at 610 mμ; 10 cm tubes
Temperature 20°

t	T	−log T	x times 10^5	a−x times 10^5	k_1	k_2
2	0.66	0.180	0.637	1.163	0.218	6.9×10^3
4	.56	.252	.891	0.909	.171	5.4
6	.46	.337	1.192	.608	.181	5.8
9	.38	.420	1.486	.314	.194	6.1
12	.31	.509	———	———	———	———
				Average	0.191	6.0×10^3

TABLE XXX

Reaction velocity of 2,6-dibromoquinonechloroimide in alkaline buffer solutions.

a = 2,6-dibromoquinonechloroimide = 1.8×10^{-5} molar

c = OH^- at pH 10.0

t = time in minutes; x = "a" transformed in "t"; T = transmittancy

The maximum absorption or final value of T = 0.31

Spectrophotometric readings at 610 mμ; 10 cm tubes

Temperature 20°

t	T	−log T	x times 10^5	a−x times 10^5	k_1	k_2
2	0.58	0.237	0.83	9.7	0.31	3.1×10^3
4	.43	.367	1.30	5.0	.32	3.2
6	.35	.456	1.61	1.9	.37	3.7
12	.31	.509	——	——	——	——
				Average	0.33	3.3×10^3

TABLE XXXI

Reaction velocity of 2,6-dibromoquinonechloroimide in alkaline buffer solutions.

a = 2,6-dibromoquinonechloroimide = 1.37×10^{-5} molar

c = OH^- at pH 9.129

t = time in minutes; x = "a" transformed in "t"; T = transmittancy

The maximum absorption or final value of T = 0.25

Spectrophotometric readings at 610 mμ. 10 cm tubes

Temperature 20°

t	T	−log T	x times 10^5	a−x times 10^5	k_1	k_2
2	0.80	0.097	0.22	1.15	(0.087)	$(6.48) \times 10^3$
3.5	.66	.181	0.41	0.96	.101	7.52
4	.62	.208	0.47	0.90	.105	7.78
6	.52	.284	0.65	0.72	.107	7.94
7.5	.42	.377	0.86	0.51	(0.132)	(9.75)
8	.39	.409	0.93	0.41	——	——
				Average	0.104	7.75×10^3

TABLE XXXII

Reaction velocity of 2,6-dibromoquinonechloroimide in alkaline buffer solutions.

a = 2,6-dibromoquinonechloroimide = 1.37×10^{-5} molar

c = OH^- at pH 9.129

t = time in minutes; x = "a" transformed in "t"; T = transmittancy

The maximum absorption or final value of T = 0.05

Spectrophotometric readings at 520 mμ. 10 cm tubes

Temperature 20°

t	T	−log T	x times 10^5	a−x times 10^5	k_1	k_2
2.33	0.58	0.237	0.25	1.12	(0.088)	(6.50) × 10^3
3	.50	.301	.32	1.05	.089	6.56
4.5	.35	.456	.48	.89	.095	7.08
5	.33	.482	.51	.86	.093	6.90
6.33	.24	.620	.65	.72	.101	7.52
7	.21	.678	.71	.66	(.104)	(7.73)
8.33	.14	.854	.90	.47	——	——
				Average	.095	7.01 × 10^3

TABLE XXXIII

Reaction velocity of 2,6-dibromoquinonechloroimide in alkaline buffer solutions.

a = 2,6 dibromoquinonechloroimide = 1.37×10^{-5} molar

a = OH^- at pH 9.528 = 3.39×10^{-5} molar

t = time in minutes; x = "a" transformed in "t"; T = transmittancy

The maximum absorption or final value of T = 0.05

Spectrophoometric readings at 520 mμ. 10 cm tubes

Temperature 20°

t	T	−log T	x times 10^5	a−x times 10^5	k_1	k_2
2	0.35	0.456	0.48	0.89	0.216	6.37 × 10^3
3.25	.21	.678	.71	.66	.225	6.63
4	.16	.796	.84	.53	.237	6.99
5.33	.116	.936	.99	.38	.240	7.09
6	.094	1.027	——	——	——	——
7.33	.08	1.097				
				Average	0.229	6.77 × 10^3

TABLE XXXIV

Summary of reaction velocity data of 2,6-dibromoquinonechloroimide in alkaline buffer solutions from Tables XXVII-XXXIII, inclusive.

Table No.	pH	Readings at wave length	Molarity of 2,6-dibromo-quinone-chloroimide	$k_1 = \frac{2.3026}{t} \log \frac{a}{a-x}$	$k_2 = \frac{2.3026}{tc} \log \frac{a}{a-x}$
27	8.5	610	1.8×10^{-5}	0.021	6.5×10^3
28	9.0	610	1.8	.058	5.8
29	9.5	610	1.8	.191	6.0
30	10.0	610	1.8	.33	3.3
31	9.129	610	1.37	.104	7.75
32	9.129	520	1.37	.095	7.01
33	9.528	520	1.37	.229	6.77
				Average	6.2×10^3

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24B-129

THE OPTICAL IDENTIFICATION OF THE NAPHTHALENE SULFONIC ACIDS BY MEANS OF THEIR BENZYL-PSEUDO-THIOUREA SALTS[1]

BY RAYMOND M. HANN AND GEORGE L. KEENAN

Introduction

The purpose of this paper is to report the optical data which are of value for determinative purposes of a number of isomeric naphthalene sulfonic acids.

Attention has been called to the usefulness of the petrographic microscope by Chamot[2] and Wright[3], and the successful application of the immersion method to the study of inorganic and organic crystalline substances has been demonstrated by Fry[4], Wherry[5,6,7], Keenan[8], and Keenan and Hann[9].

Optical Examination

The optical examination of crystalline material may be conveniently divided into three parts, namely, in ordinary light (using one nicol prism), in parallel polarized light (crossed nicols), and in convergent polarized light (crossed nicols).

In ordinary light the microscope reveals the form or habit of the crystalline material and enables the refractive indices to be determined. The method, as commonly employed by petrographers for the identification of rock fragments, involves the immersion of the crystalline material in a drop of liquid (usually oily in nature) the refractive indices of which have been previously determined on a refractometer.

The liquids most suitable are mixtures of mineral oil ($n=1.49$), monochlornaphthalene ($n=1.64$), monobromnaphthalene ($n=1.66$) and methylene iodide ($n=1.74$). For ordinary purposes these oils are mixed in such proportions that each differs in refractive index from the next by an increment of 0.005. Observations are usually made in monochromatic light, approximating that of the D-line, most conveniently obtained by interposing a yellow glass or gelatine film between a source of brilliant white light and the microscope mirror.

For the determination of the refractive indices, the crystals or crystal fragments of a given substance are successively suspended in these liquids,

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[1] Contribution from Bureau of Chemistry, U. S. Department of Agriculture. Presented before Los Angeles meeting of Am. Chem. Soc., Aug. 3-8 (1925).

[2] E. M. Chamot: "Elementary Chemical Microscopy" (1921).

[3] F. E. Wright: J. Am. Chem. Soc., **38**, 1647 (1916).

[4] W. H. Fry: U. S. Dept. Agric. Bul., **97**, (1914).

[5] E. T. Wherry: U. S. Dept. Agric. Bul., **679** (1918).

[6] G. S. Jamieson and E. T. Wherry: J. Am. Chem. Soc., **42**, 136 (1920).

[7] J. A. Ambler and E. T. Wherry: J. Ind. Eng. Chem., **12**, 1086 (1920).

[8] G. L. Keenan: J. Biol. Chem., **62**, 163 (1924).

[9] G. L. Keenan and R. M. Hann: J. Am. Chem. Soc., **47**, 2063 (1925).

advantage being taken of the fact that the greater the difference between the indices of refraction of crystal and liquid, the more prominently the one will stand out from the other. By repeatedly mounting such crystals in oils of successively lower or higher index, it will be found that ultimately the zone of contact of crystal with liquid becomes practically invisible, and then the refractive index has been matched. In the case of substances crystallizing in the isometric (cubic) system, there is only one refractive index. Such substances are not doubly refractive when examined with crossed nicols (parallel polarized light). Substances crystallizing in other systems have more than one refractive index, and with them the position of the grain with reference to the vibration plane of the nicol prism must be taken into account.

In any case, when the contact of the liquid with the crystal becomes invisible, the n-value of the crystal and of the liquid are identical in that crystallographic direction in which the light is then vibrating. By bringing the crystals into other positions with reference to the plane of vibration of the nicol and successively mounting in other liquids, two or three different n-values of the crystals of a given substance can be obtained. Usually two such values are sufficient for the identification of the substance, but a third value may often be determined. Substances crystallizing in the orthorhombic, monoclinic, and triclinic systems usually show three significant refractive index values, designated as n_α, n_β, and n_γ.

In parallel polarized light (crossed nicols) it may be ascertained whether the material is isotropic or doubly refractive. Isotropic substances transmit no light when examined with crossed nicols. Doubly refractive or anisotropic substances, on the other hand, do transmit light under the same conditions and exhibit changes from light to dark when the stage is rotated. The extinction may occur when a prominent zone of edges is parallel to the vibration plane of one of the nicols, or at a definite angle thereto.

In convergent polarized light (crossed nicols) it is possible to determine whether the substance is uniaxial or biaxial, which may assist in ascertaining the system in which the substance crystallizes. Other optical properties can be determined with convergent polarized light, but these are not as important for determinative purposes as the refractive indices.

Experimental

The value of benzyl-pseudo-thiourea salts as reagents for the identification of organic acids has been indicated by Donleavy and Johnson[1]. The specific application of this procedure to the identification and purification of certain of the naphthalene sulfonic acids has been made by Chambers and Scherer[2].

We have prepared a number of such salts, analyzed the compounds obtained, subjected the derivatives to optical examination and prepared photomicrographs of those showing a characteristic crystalline structure.

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[1] J. J. Donleavy and T. B. Johnson: Science, **57**, 753 (1925). Abstract of a paper read at the New Haven Meeting of the American Chemical Society, April 2-7, 1923.

[2] R. F. Chambers and P. C. Sherer: Ind. Eng. Chem., **16**, 1272 (1924).

Benzyl -ψ- thiourea hydrochloride

This salt was prepared from thiourea and benzyl chloride according to Werner's[1] modification of the method of Bernthsen and Klinger[2].

No hydrochloric acid was evolved, but all was reabsorbed, and it is the hydrochloride, not the free benzyl-ψ-thiourea, which separates from the reaction mixture. The crude material was recrystallized from 0.2 *N* hydrochloric acid and obtained as clear, colorless needles which melt at 176°C, (cor.) Werner reports 174° and Bernthsen and Klinger 166-8°C. Analysis (Kjeldahl-Gunning-Arnold Method) 13.83% N. Theory for $C_8H_{11}SN_2Cl$ is 13.83% N.

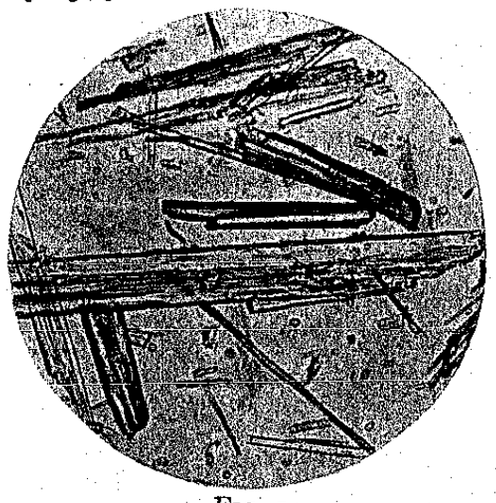


FIG. 1
Benzyl- ψ-thiourea salt of α naphthalene sulphonic acid.
(×90)

Optical Properties

Crystal habit.—In ordinary light under the microscope, the material was found to be fibrous or rod-like in habit.

Refractive indices.— $\frac{(20°)}{(D)} - n_\alpha = 1.631$, shown crosswise on elongated grains but not common; $n\beta = 1.683$, crosswise; $n_\gamma = 1.689$, shown lengthwise and very common; all ± 0.002. (Checked by a monochromatic illuminator).

Characters shown in parallel polarized light with crossed nicols.—The double refraction is strong, $n_\gamma - n_\alpha = 0.058$; extinction parallel; elongation +.

Characters shown in convergent polarized light with crossed nicols.—None.

Distinctive characters.—The fibrous, rod-like habit is somewhat characteristic for the substance, but the maximum refractive index value, which always occurs lengthwise, is significant.

Benzyl -ψ- thiourea salt of α-naphthalene sulfonic acid (Fig. 1)

Equivalent weights of the sulfonic acid and benzyl-ψ-thiourea hydrochloride were separately dissolved in warm 0.2 *N* hydrochloric acid and the warm solutions mixed. The salt separated as the solution cooled in colorless flower-like clusters of crystals. These were filtered off by suction, washed with water and dried. Upon a slow heating in a capillary tube the crystals melted at 138°C., a short range Anschütz thermometer being used as a standard. Analysis: 7.46% N. Theory for $C_{13}H_{18}O_3N_2S_2$ is 7.48% N.

Optical Properties

Crystal habit.—When examined in ordinary light under the microscope the substance was seen to consist of rods.

Refractive indices.— $\frac{(20°)}{(D)-} - n_\alpha = 1.611$, not common and occurring

[1] E. A. Werner: J. Chem. Soc., **57**, 285 (1890).
[2] A. Bernthsen and H. Klinger: Ber., **12**, 574 (1879).

crosswise on rods; $n_\beta = 1.672$, shown lengthwise and very common; $n_\gamma = 1.680$, shown crosswise; all ± 0.002. (Checked by a monochromatic illuminator).

Characters shown in parallel polarized light with crossed nicols.—The double refraction is strong, $n_\gamma - n_\alpha = 0.069$; extinction parallel; elongation $\pm$.

Characters shown in convergent polarized light with crossed nicols.—Partial biaxial interference figures frequent, showing but one optic axis up.

Distinctive characters.—The most characteristic feature of this substance appears to be the value $n_\beta = 1.672$, which is readily found.

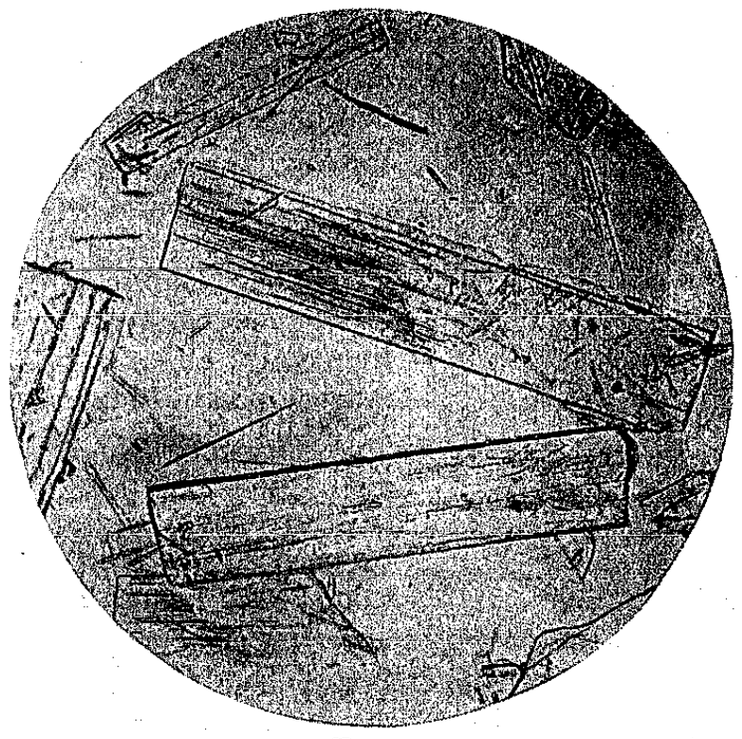


FIG. 2
Benzyl- ψ-thiourea salt of β naphthalene sulphonic acid. (×90)

Benzyl -ψ- thiourea salt of β-naphthalene sulfonic acid (Fig. 2)

The beta isomer was prepared in a similar manner from β-naphthalene sulfonic acid. After recrystallization from 0.2 *N* hydrochloric acid this salt melted at 193°C. to a clear oil. Analysis: 7.55% N. Theory for $C_{18}H_{18}O_3N_2S_2$ is 7.48% N.

Optical Properties

Crystal habit.—In ordinary light, the material was seen to consist of rods, many having oblique terminations.

Refractive indices.—$\frac{(20°)}{(D)} - n_\alpha = 1.577$, common and occurring on rods crosswise; $n_\beta = 1.590$; $n_\gamma = 1.682$, occurring lengthwise, all ± 0.002. (Checked by a monochromatic illuminator).

Characters shown in parallel polarized light with crossed nicols.—The double refraction is extreme, $n_\gamma - n_\alpha = 0.105$; extinction parallel; elongation +.

Characters shown in convergent polarized light with crossed nicols.—Partial biaxial interference figures rarely shown.

Distinctive characters.—The value $n_\gamma = 1.682$ occurs frequently on rods lengthwise, and is significant for purposes of identification.

Benzyl -ψ- thiourea salt of 1:5 naphthalene disulfonic acid

This substance separated from solution in slightly yellow aggregates of block-like crystals. Upon slow heating in a capillary tube it melted at 251°C. (cor.) with spontaneous decomposition. Analysis: 8.74% N. Theory for $C_{26}H_{28}O_6N_4S_4$ is 9.03% N.

Optical Properties



FIG. 3
Benzyl- ψ-thio salt of 2.6 naphthalene disulphonic acid.
(×170)

Crystal habit.—The material when examined under the microscope in ordinary light was found to consist of irregular fragments.

Refractive indices.— $\frac{(20°)}{(D)} - n_\alpha = 1.580$ common; $n_\beta = 1.670$ measurable on fragments, showing one optic axis up in the interference figure; $n_\gamma = 1.690$, occurring frequently; all ± 0.002. (Checked by a monochromatic illuminator).

Characters shown in parallel polarized light with crossed nicols.—Double refraction extreme, $n_\gamma - n_\alpha = 0.110$; many fragments show third and fourth order colors; color bands distinct.

Characters shown in convergent polarized light with crossed nicols.—The greater portion of the fragments extinguish sharply in parallel polarized light (crossed nicols), so that good interference figures would not be expected, but occasional fragments show one optic axis up; optic sign −.

Distinctive characters.—The most diagnostic refractive index for this substance is $n_\gamma = 1.690$, shown frequently on fragments extinguishing sharply in parallel polarized light (crossed nicols).

Benzyl -ψ- thiourea salt of 2:6 naphthalene disulfonic acid (Fig. 3)

The salt of the disulfonic acid separated in soft, glistening micaceous crystals from a solution containing its components in molecular proportions. It melted[1] at 256°C. (cor.). This melting point was taken by Mr. J. F. Clevenger in the micro-melting point apparatus described in Ind. and Eng. Chem., *16*, 854 (1924). Analysis: 8.86% N. Theory for $C_{26}H_{28}O_6N_4S_4$ is 9.03% N.

Optical Properties

Crystal habit.—When examined under the microscope in ordinary light, the substance was found to consist of rods and needles.

[1] Chambers and Scherer (loc. cit.) report 200°C. (uncorrected). In a private communication, Dr. Chambers states that this report was due to a clerical error and a redetermination of the melting point shows their sample to melt at 258°C. (uncorrected).

Refractive indices.— $\frac{(20^\circ)}{(D)} - n_\alpha = 1.570$, common and occurring on rods and needles crosswise; $n_\beta = 1.585$; $n_\gamma = 1.670$, shown lengthwise, all ± 0.002. (Checked by a monochromatic illuminator).

Characters shown in parallel polarized light with crossed nicols.—The double refraction is extreme, $n_\gamma - n_\alpha = 0.100$; extinction essentially parallel; elongation +.

Characters shown in convergent polarized light with crossed nicols.—Partial biaxial interference figures rarely shown.

Distinctive characters.—Two values, $n_\alpha = 1.570$ and $n_\gamma = 1.670$, are both readily found. The latter is partially useful for determinative purposes.

Benzyl -ψ- thiourea salt of 2:7 naphthalene disulfonic acid

Three grams of the sodium salt of 2:7 naphthalene disulfonic acid was dissolved in 25 cc. of 0.2 *N* hydrochloric acid and a hot solution of 2 gms. of benzyl-ψ-thiourea in 25 cc. of 0.2 *N* hydrochloric acid was added. The resultant salt solution was filtered rapidly and upon cooling the salt crystallized out. It was filtered by suction and recrystallized from 0.2 *N* hydrochloric acid. It was finally obtained as colorless, shining leaf-like crystals, which melted when slowly heated at 211-2°C. (cor.) with some decomposition. Analysis: 8.75% N. Theory for $C_{26}H_{28}O_6N_4S_4 \cdot 1H_2O$ is 8.77% N.

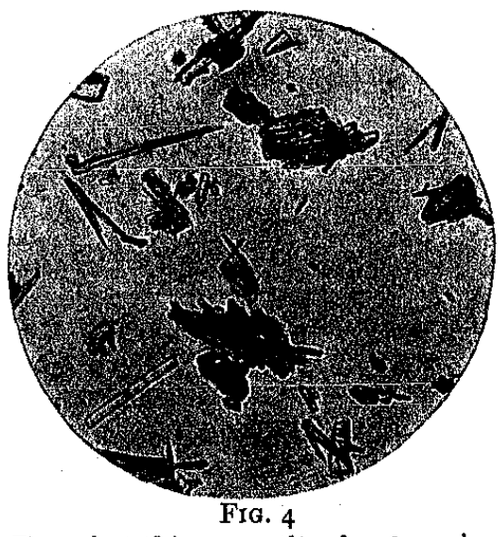


FIG. 4
Benzyl-ψ-thiourea salt of 1.6 naphthalene disulphonic acid.
(×170)

Optical Properties

Crystal habit.—In ordinary light, this material was found to consist of irregular fragments and thin, six-sided plates.

Refractive indices.— $\frac{(20^\circ)}{(D)} - n_\alpha = 1.570$, not common; n_β = indeterminable; $n_\gamma = 1.645$, occurring frequently; both ± 0.002. (Checked by a monochromatic illuminator).

Characters shown in parallel polarized light with crossed nicols.—The double refraction is strong, $n_\gamma - n_\alpha = 0.075$; third and fourth order colors shown.

Characters shown in convergent polarized light with crossed nicols.—Biaxial figures occur occasionally, sometimes perpendicular to acute bisectrix; optic axial angle indicated to be large, approximately 100°; optic sign +.

Distinctive characters.—The value $n_\gamma = 1.645$, being most readily found, is considered most significant for diagnostic purposes.

Benzyl -ψ- thiourea salt of 1:6 naphthalene disulfonic acid (Fig. 4)

Three grams of pure barium salt[1] of 1.6 naphthalene disulfonic acid was dissolved in 50 cc. of hot water and 26.7 cc. of normal sulfuric acid was added to the solution. The precipitated barium sulfate was filtered off and the filtrate was treated with a solution of 2 gms. of benzyl-ψ-thiourea hydrochloride in 25 cc. of 0.2 *N* hydrochloric acid. The acid solution was concentrated to a volume which allowed cooling without the separation of oily material and was seeded with seed crystals of the 1:6 salt. An abundant crop of perfectly colorless crystals separated on standing overnight. These were filtered by suction and dried. Upon heating in a capillary tube they began to decompose at 81°C. with loss of water. Analysis: 8.39% N. Theory for $C_{26}H_{28}O_6N_4S_4 \cdot 4H_2O$ is 8.31% N.

Optical Properties

Crystal habit.—Examined in ordinary light, the material consisted of rods and irregular fragments.

Refractive indices.— $\frac{(20°)}{(D)}$ $n_\alpha = 1.565$, crosswise on rods, also on irregular fragments; $n_\beta = 1.580$ crosswise; $n_\gamma = 1.670$, lengthwise, common; all $\pm$ 0.002. (Checked by a monochromatic illuminator).

Characters shown in parallel polarized light with crossed nicols.—Double refraction extreme $n_\gamma - n_\alpha = 0.105$; extinction parallel; elongation +.

Characters shown in convergent polarized light with crossed nicols.—None.

Distinctive characters.—The value likely to be of most significance in identifying the substance is the maximum refractive index, $n_\gamma = 1.670$. This occurs frequently and is found lengthwise on rods.

Method of Identification

For rapid identification of the salts described, a determinative table (Table I) has been prepared. In order to use this table crystalline material is to be immersed successively in the liquids of refractive indices shown in the left-hand column. Upon examination under the microscope with polarizer in place and diaphragm partially closed, trying one liquid after another, the outlines of the fragment disappear when its refractive index in one position of the field has been matched. Confirm identity of the substance by the data in the central column, and obtain the name of the compound in the right-hand column.

The data which have been obtained are brought together in Table II.

[1] For the sodium and barium salts of 2:7 and 1:6 naphthalene disulfonic acids we are indebted to Mr. John Scanlon, Bureau of Chemistry.

TABLE I

Determinative Data

Index	Description of crystals and confirmatory data	Compound
1.570	Material consists of rods and needles examined in ordinary light. This index value is shown crosswise on rods and needles. Confirm by immersing in liquid 1.670, which matches γ shown lengthwise on rods and needles.....	2:6
1.645	When examined in ordinary light the material consists of irregular fragments and thin, six-sided plates. Confirm by immersing in liquid 1.570, which matches α.....	2:7
1.670	Material consists of rods and irregular fragments when examined in ordinary light. This value is commonly found lengthwise on rods. Confirm by immersing in liquid 1.565 which matches α and is shown crosswise on rods.....	1:6
1.672	The material consists of rods when examined in ordinary light. This value is commonly found and occurs lengthwise on rods. Confirm by immersing in liquid 1.680, which matches γ and is shown crosswise on rods.....	α
1.682	Material in ordinary light consists of rods, many of which have oblique terminations. This index value occurs lengthwise on rods. Confirm by immersing in liquid 1.577, which matches α shown frequently crosswise on rods.....	β
1.689	Material in ordinary light consists of fibrous, rod-like crystals. This index matches γ. Confirm by immersing substance in liquid 1.631, which matches α and is shown crosswise.....	Hydrochloride.
1.690	Material consists of irregular fragments when examined in ordinary light. This index value is shown on fragments extinguishing sharply in parallel polarized light (crossed nicols). Confirm by immersing in liquid 1.670, which matches β and is frequently shown.....	1:5

TABLE II
Optical Features of Compounds described

	2:7	1:6	2:6	1:5	Hydrochloride	α	β
Habit	plts.	rds.	rds.	plts.	rod-like	rds.	rds.
Indices:							
n_α	1.570	1.565	1.570	1.580	1.631	1.611	1.577
n_β	indt.	1.580	1.585	1.670	1.683	1.672	1.590
n_γ	1.645	1.670	1.670	1.690	1.689	1.680	1.682
$n_\gamma - n_\alpha$	0.075	0.105	0.100	0.110	0.058	0.069	0.105
Significant	1.645	1.670	1.570	1.690	1.689	1.672	1.682
Extinction	indt.	par.	par.	indt.	par.	par.	par.
Elongation	indt.	+	+	indt.	+	±	+
Figures	freq.	o	rare.	occas.	o	freq.	rare.
2E	100°		indt.	indt.	indt.	indt.	indt.
Sign	+	indt.	indt.	—	indt.	indt.	indt.

Summary

Optical data on the benzyl-ψ-thiourea salts of a number of naphthalene sulfonic acids have been determined and the results tabulated in a form suitable for rapid identification by microscopic observation.

2-190

COLLOIDAL IODINE[1]

BY WALLACE L. CHANDLER AND ELROY J. MILLER

The literature on the chemistry of iodine contains but few references to researches dealing with the colloidal state or colloidal behavior of this element. It is replete, however, with reports on studies pertaining to iodine combined with or adsorbed by substances such as starches, proteins, tannins, and charcoal. These combinations are sometimes termed colloidal iodine but they are in reality either true iodine compounds or adsorbents carrying adsorbed iodine.

Among the researches dealing with iodine in a truly colloidal state are those of Amann.[2] He observed that fresh alcoholic iodine solutions show the Tyndall effect. He also observed with the aid of the ultramicroscope the formation of solutions of iodine in carbon disulfide, chloroform, carbon tetrachloride, toluene, xylene, and other solvents. In carbon disulphide, carbon tetrachloride, and chloroform the iodine was in true solution as shown by the absence of ultramicropscopic particles. In toluene and xylene, however, there appeared suddenly clouds of particles in lively Brownian movement. In water the formation of micellae preceded the formation of crystals. Neither the organosols nor the hydrosols were stable. Hydrosols of iodine were also prepared by Harrison[3] by the interaction of hydriodic and iodic acids. The blue sols formed in this manner were unstable, turning gray and flocculating almost instantly. Holmes and Williams[4] in a study of iodine as an emulsifying agent conclude that iodine functions as an emulsifying agent by virtue of the formation of colloidal aggregates at the liquid-liquid interface. Bordier and Roy[5] presented evidence to show that iodine in water at 0° is in aggregates made up of more than two atoms. By the addition of a concentrated alcoholic solution of iodine to 0.4% gelatine solution they obtained a colloidal solution that contained 0.4% iodine. In 1925 one of us[6] announced the production of a fairly stable suspensoid of iodine by the interaction of hydriodic acid and a hypohalous acid in dilute solution at 0° in the presence of gum arabic.

It is the purpose of this paper to describe methods for the preparation of relatively stable aqueous colloidal suspensions of iodine.

Precipitation of Iodine from Solutions

Formation of unstable suspensions. In the rapid precipitation of iodine from solutions in organic solvents or aqueous salt solutions there is formed a brick red suspension. This suspension is extremely unstable and changes

[1] Contribution from the Bacteriological and Chemical laboratories of the Michigan Agricultural Experiment Station. Published by permission of the Director of the Experiment Station as journal article No. 40.

[2] Kolloid-Z., **6**, 235 (1910); **7**, 67 (1910); Kolloidchem. Beihefte, **3**, 337 (1912).

[3] Kolloid-Z., **9**, 5 (1911).

[4] "Colloid Symposium Monograph", **2**, 138 (1925).

[5] Compt. rend., **163**, 567 (1916).

[6] Chandler: Proceedings Twenty-ninth Annual Meeting of the U. S. Live Stock Sanitary Association (1925).

almost instantly into a dark precipitate that quickly settles out. This phenomenon may be brought about in a number of ways, as, for example, by the acidification with a strong acid of a dilute solution of a mixture of iodide and iodate, by the precipitation of iodine from solution in absolute alcohol or glacial acetic acid through the rapid addition of these solutions to cold water, or, in general, by producing suddenly a highly supersaturated solution of iodine in water.

Formation of stable suspensions. The possibility of stabilizing the brick red suspension of iodine was suggested. While the probability of stabilizing this suspension successfully seemed rather remote because of the exceedingly rapid growth of the small particles into coarse crystals a number of the more common substances known to possess protective properties were, nevertheless, tried out. Gum arabic proved to be fairly satisfactory so that under certain conditions relatively stable suspensions were formed. In working with these suspensions it became apparent that certain conditions must obtain in order to produce the most satisfactory stabilization. It was necessary (in accordance with von Weimarn's principle) that the production of the supersaturation be exceedingly rapid in order to insure the formation of the smallest particles. It also seemed necessary to keep the temperature in the neighborhood of 0°, possibly in order to delay the growth of the particles and permit time for the formation of the protective coating around them.

In this manner a purplish suspension of fairly small crystals was formed when dilute solutions of sodium iodide and sodium iodate in the proportions of five to one were acidified rapidly in the cold in the presence of gum arabic.

$$2HCl + NaI + NaIO_3 \longrightarrow 2NaCl + HI + HIO_3$$

$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

The oxidation of the hydriodic acid by the iodic acid with the formation of free iodine was apparently rapid enough to produce minute crystals but it was not sufficiently rapid to produce a large amount of very fine particles for the precipitated iodine remained in suspension only a few minutes. Microscopic examination showed the precipitate to be largely in the form of small crystals but a small portion consisted of very minute globular particles. These will be described in detail later.

A suspension of much greater stability was formed under similar conditions by employing the oxidation of hydriodic acid by hypoiodous acid for the rapid production of the high supersaturations.

$$Na_2I(OI) + 2HCl \longrightarrow 2NaCl + HI + HOI$$

$$HI + HOI \longrightarrow I_2 + H_2O$$

Sodium iodohypoiodite is easily prepared for this purpose by rapidly treating a one to two per cent solution of sodium hydroxide with iodine until the straw-colored liquid, which forms immediately, just begins to turn red and then pouring this solution from the remaining iodine crystals.

$$2NaOH + I_2 \longrightarrow Na_2I(OI) + H_2O$$

This dilute solution of sodium iodohypoiodite appears to be stable for several hours provided it is removed without delay from the excess of iodine. In time, however, the hypoiodite changes into the iodide and iodate.

$$_3Na(OI) \rightleftarrows {}_2NaI + Na(IO_3)$$

When a more concentrated solution of sodium hydroxide is treated with iodine the iodate is formed immediately. If this concentrated solution is heated until the iodate crystals all dissolve and at once diluted with water the hypoiodite is again produced, for the above reaction is reversible.

The rapid acidification with concentrated hydrochloric acid of a dilute solution of sodium iodohypoiodite in the presence of gum arabic at 0° produces a relatively very stable suspension. Its color varies somewhat with the conditions of formation. It may be brick red, light brown, or ground chocolate. When prepared under favorable conditions it remains in suspension for several weeks without showing any appreciable settling. On standing for some months however, there is a tendency for the suspension to settle and a clear straw-colored supernatant solution begins to appear. Specimens of preparations that have stood from eighteen to twenty one months show considerable settling, but their structure remains apparently unchanged. When viewed through the microscope they were found, like the fresh preparations, to be made up of the small globules in rapid Brownian motion. The material was easily dispersed again by shaking once or twice.

Nature of the Suspension

When examined under the microscope the suspension was found to be made up almost exclusively of minute globules in rapid Brownian movement. The largest globules were approximately 0.2 micron in diameter and surprisingly uniform in size. There were, however, many smaller globules and possibly some were of ultramicroscopic dimensions for the largest ones were just resolvable under the highest power of the microscope (1500 times). The larger globules were unmistakably spherical in shape and the smaller ones were presumably so. This suggested that the suspension might be an emulsoid with liquid iodine the disperse phase and a saturated solution of iodine in water the dispersion medium. Further evidence of the emulsoid nature of the system is found when the process of formation of the particles is observed under the microscope. The procedure may be conveniently carried out in the following manner: A drop of dilute solution containing a mixture of a metal iodide and iodate in the proportions stated above is placed under a coverslip on a glass slide. The solution is then brought approximately in focus and a drop of hydrochloric acid is placed at the edge of the coverslip. As the acid diffuses into the solution under the coverslip there appears a yellow area (by transmitted light) where the iodine is formed. Immediately behind this yellow area appears a swarm of iridescent globules in rapid Brownian movement and directly behind these globules there are formed small diamond-shaped crystals of iodine. With a movable stage the progress of the diffusion of the acid can readily be followed. When the progress of the diffusion is rapid, as when the acid is first touched to the edge of the coverslip, the swarm

of globules always appears just behind the yellow area and the crystals always appear behind the globules. But, when the progress of the diffusion becomes slower the globules cease to appear and the crystals form immediately behind the yellow area. This is in keeping with the fact that it is essential that a rapid mixing take place for the production of the brick-red suspension. The mechanism of the action is probably as follows: The yellow area represents a highly supersaturated solution of iodine. The iodine in excess of the amount necessary for saturation is thrown out in the form of globules of liquid iodine since there is not time for molecular orientation necessary for the formation of crystal structure. These globules of liquid iodine are in equilibrium with a saturated aqueous solution of iodine. From the saturated iodine solution crystallization begins and since the vapor pressure of the liquid is undoubtedly higher than that of the crystals, the globules go into solution as fast, or nearly so, as the crystallization removes iodine from solution. When the higher supersaturation is not reached, as is the case when the diffusion of the acid into the salt solution is slow, the iodine is liberated slowly enough so that the crystallization is sufficient to remove the excess of iodine without the formation of the liquid globules.

The presence of gum arabic in the salt solution before acidification changes radically the picture just presented. The yellow area appears as does also the swarm of globules but no crystals are formed. The globules are stabilized and remain in suspension.[1] This is the brick red to brownish suspension obtained in quantity as above described. When the protective colloid is absent, the brick red appearance quickly changes to purplish due to the formation of the minute crystals of iodine. Thus the evidence obtained microscopically substantiates and amplifies the conclusions arrived at from the work with the solutions in larger quantities. It might be mentioned in passing that a macroscopic observation of the diffusion of the acid into the salt solution under the coverslip shows in the absence of the gum arabic a steel blue area where the acid has penetrated. In the presence of gum arabic this area is brick red or brown. There is, therefore, considerable evidence that we are dealing with an emulsoid system in which the globules of liquid iodine are suspended in a saturated aqueous solution of iodine.

Preparation of Concentrated Emulsions

As previously stated, the particles making up the emulsoid are for the most part small and of the order of 0.2 micron or less in diameter. They readily pass through filter paper and through Berkefeld filters. After the first few seconds of filtration through a Chamberlain filter, however, they are held and the emulsion may be concentrated somewhat in this manner by forced filtration. The concentrating of the emulsion does not seem to affect markedly its stability. Attempts at concentration by centrifuging were not successful. Standing for a number of weeks or months results in a partial

[1] This appears to be experimental verification of the theoretical considerations stated by Wo. Ostwald. See Ostwald-Fischer: "Handbook of Colloid Chemistry", Second Edition, page 63.

concentration in the lower part of the containing vessel and the saturated aqueous iodine solution may be drawn off. Evaporation obviously results in the loss of iodine since the dispersion medium is a saturated solution of iodine in water. The volatility of the iodine thus prevents the successful concentration of the emulsion by this method.

A method was found, however, whereby the emulsions could be greatly concentrated and even dried. This method consisted essentially of the formation of a thick syrup by the addition of dextrose or gum arabic to the emulsion. From this syrup the water could readily be evaporated with but little or no loss of iodine. A film or membrane forms on the surface of the syrup. This film permits the evaporation or loss of water molecules, but not of the iodine molecules. The evaporation may be allowed to continue until a hard brittle mass remains. Drying does not cause the particles of iodine to fuse together or coalesce and the particles readily disperse again to form an emulsion when the solid is shaken up in water.

The syrup may be spread out in thin layers and quickly dried after which it may be powdered. When it is powdered a small amount of iodine is given off, probably due to the fracturing of the protective coating of some of the particles with the consequent exposure of iodine. If the exposed iodine is driven off by the application of gentle heat the remainder of the iodine is perfectly stable, so stable in fact that the powder has little or no odor of iodine and may be kept in paper containers without staining the paper.

Additional evidence of the structure of this colloidal iodine system is obtained from the behavior of this powder or the concentrated emulsion when added to water and alcohol. When either the emulsion or the powder is added to water the iodine goes in solution quickly and forms a saturated solution of iodine in water. A saturated aqueous solution of iodine ordinarily requires several days for formation from ordinary crystalline iodine owing to the slight solubility of iodine (0.034% at 25°). With the emulsoid, however, the production of a saturated solution is almost instantaneous due undoubtedly to the fact that such small particles have a higher vapor pressure or solution pressure and a lower surface tension than the same material in a coarser state. Since iodine is readily soluble in alcohol it might at first thought be expected that the addition of the emulsoid or the powder would likewise result in the rapid formation of a concentrated solution of iodine in alcohol. Such, however, is not the case. The colloidal iodine goes in solution more slowly in alcohol than in water and is accompanied by the flocculation and settling out of the gum arabic. This would seem to be explainable on the basis that the gum arabic functioning as a protective colloid and forming a coating around the iodine must first be flocculated before the alcohol can come in contact with the iodine. In keeping with this explanation chloroform does not extract iodine from the dry stabilized powder, that is, the powder that has been heated to drive off the iodine exposed in grinding. If, however, the powder is first wetted with water, then the chloroform extracts the iodine from the aqueous solution. At the same time more of the colloidal iodine dissolves to maintain a saturated aqueous solution. This process continues until practically all the iodine has passed into the chloroform.

Value of Colloidal Iodine as an Antiseptic and Disinfectant.

Brief mention of a few of the properties of colloidal iodine as an antiseptic and disinfectant may not be out of place at this point. Unlike alcoholic solutions of iodine, the aqueous suspension of iodine is practically non-irritating when applied to fresh wounds and it is at the same time free from injurious effects of alcohol on living tissue. When applied to the skin it produces a stain but does not blister unless the application is unnecessarily heavy and prolonged. The intensity of the stain is easily controlled, for whatever the quantity of iodine in suspension the solution in contact with the skin is only the 0.034% solution of iodine in water. This concentration of iodine in water is amply sufficient for all germicidal purposes and yet not sufficient to corrode the skin or tissues as does the alcoholic solution. Furthermore, the 0.034% solution is maintained practically constant as long as there is any of the colloidal iodine in suspension for the iodine removed from the solution by the skin or tissues is immediately replaced by the dissolving of some of the emulsoid iodine. The stain, unlike that produced by alcoholic iodine, disappears rapidly and completely within a few hours. Since water offers the most convenient medium for bringing disinfectants in contact with microorganisms, the advantages of the emulsoid in the powdered form for convenience in carrying are obvious. It is only necessary to add the powder to water and even water is not absolutely essential, for the powder may be dusted directly on wounds. The water from the serum is sufficient to liberate iodine from the powder. Still another way in which the colloidal iodine may be conveniently used is in the form of applicators. These applicators may easily be prepared by dipping one end of wooden, glass, or even metal sticks or rods in the above mentioned thick syrup and drying.

Summary

1. Methods have been described for the preparation of colloidal iodine.

2. Evidence has been presented to show that iodine may be brought into the form of an emulsion in water. This emulsion is capable of existing only momentarily.

3. By means of protective colloids the emulsion may be rendered stable.

4. Methods of concentrating this emulsion have been described.

5. The concentration of this emulsion may be carried out to the extent of bringing it into a dry condition without impairing its ability to redisperse in water.

6. A few of the possible uses and advantages of colloidal iodine as an antiseptic have been pointed out.

East Lansing, Michigan.

SOCIETE DE CHIMIE INDUSTRIELLE
S-Dominique
28, RUE
PARIS (7e)

A NEW THERMOREGULATOR

BY S. C. COLLINS

The thermoregulator described is operated directly by 110-volt alternating current without the use of dry cells and sensitive relay. The heating effect is produced by passing the electric current through the water bath itself, the water being made conducting by addition of salt. The sensitive member depends for its motion upon the differential expansion of the saturated vapor of ether or other liquid and air. The heating current is applied continuously and is adjusted by an automatic rheostat to a value that will just compensate for heat losses. Since the circuit is never broken, no difficulty from arcing is experienced.

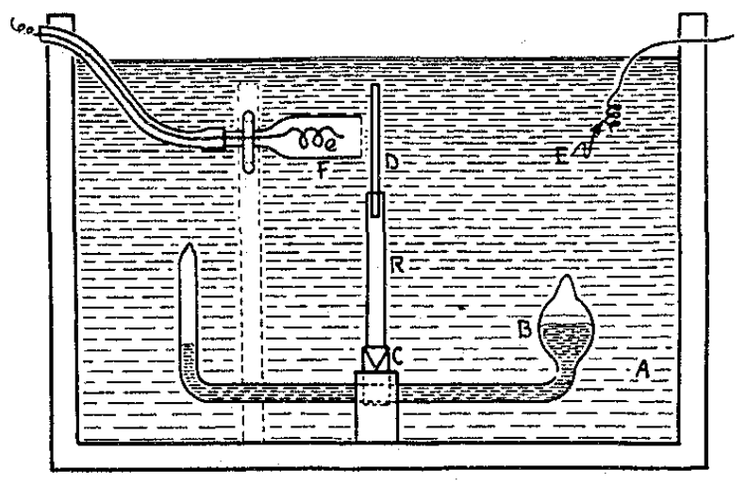


FIG. 1
Sectional View of Thermoregulator

The maximum variation in temperature under average operating conditions can be expected not to exceed .02 degree C.

Referring to the figure, A is an insulated tank containing the water in which the regulating device is submerged. An ordinary galvanized wash boiler was used by the author. B represents the sensitive member. It is made from a glass tube 1 cm. in diameter and about 20 cm. long and contains a layer of ether or other liquid above mercury in one end and air above mercury in the other. The tube is supported in a horizontal position between two blocks by means of two metal points, C, only one of which is shown in the diagram. The point of suspension is just above the center of gravity of the tube and its contents. The point bearings may be obtained by bending a strip of brass to proper shape and filing the ends. The same strip of brass serves to clamp the sensitive member to the wooden rod, R, which extends vertically upwards. R is about 10 cm. long and 1 by 4 cm. in cross section. It carries at its upper end a glass plate, D, 6 by 6 cm. D, therefore, rotates with the tube about the pivot, C. F is a Gooch funnel so assembled that its mouth may be completely

closed by the glass plate whenever the sensitive member is approximately horizontal. E and *e* are the electric terminals by which the alternating current enters and leaves the bath. They are made of heavy copper wire. E dips into the solution directly, while *e* is brought in through a rubber tube to the funnel.

All of the current passing between the electrodes must flow through the mouth of the funnel. Hence, if that opening is made greater or smaller, the resistance becomes less or greater respectively. In other words the column of liquid joining the two electrodes is a conductor whose resistance can be varied by infinitesimal amounts by changing the position of the glass plate, D.

In operation the temperature of the bath is brought to the desired temperature approximately and the tube, B, is slipped to and fro through its supporting mechanism until a balance is obtained. With a rising temperature the vapor pressure of the ether increases more rapidly than does the pressure of the enclosed air. Consequently the mercury shifts from one end toward the other. Shifting of the mercury destroys the balance and results in a change of the position of the glass plate in such a way that the mouth of the funnel is more nearly closed. This motion continues to take place until the current is reduced to such a value that no excess heat is produced.

In the construction of the unit, the glass tube is given the form shown in the diagram but with the air end open. A few drops of ether and afterwards mercury are placed in the tube, care being taken to displace all the air in the ether end. The open end is then heated to drive off adhering droplets of ether. Finally the tube is closed in the flame.

For temperatures between 20 and 45 degrees C. ether serves well as the working fluid. At higher temperatures, however, the excessive pressure developed makes it desirable to substitute another substance. Aqua ammonia has been found satisfactory.

This thermoregulator has been used at temperatures up to 68 degrees C. The regulation, however, is not so efficient at high temperatures.

The amount of salt used in the water varies with the temperature desired, but in no case is it necessary to add more than a few grams of salt per liter of water.

The water may be stirred by any of the ordinary stirring devices. Moderate agitation of the liquid does not interfere with the action of the regulator.

University of North Carolina,
Chapel Hill.
May, 1927.

13-188

AN ALL-GLASS GAS CIRCULATING APPARATUS*

BY W. S. FUNNELL AND G. I. HOOVER

The diagram represents a pump in use in this laboratory in connection with experiments on adsorption. The diagram is self-explanatory, and although the dimensions are arbitrary, they necessarily affect the capacity. The dimensions of our pump are as follows. The solenoids are 6.5 cm. long, 10 cm. between centres, and wound with 1200 turns of no. 23 wire on the brass tube used as a water jacket. The barrel is 40 cm. long with an internal

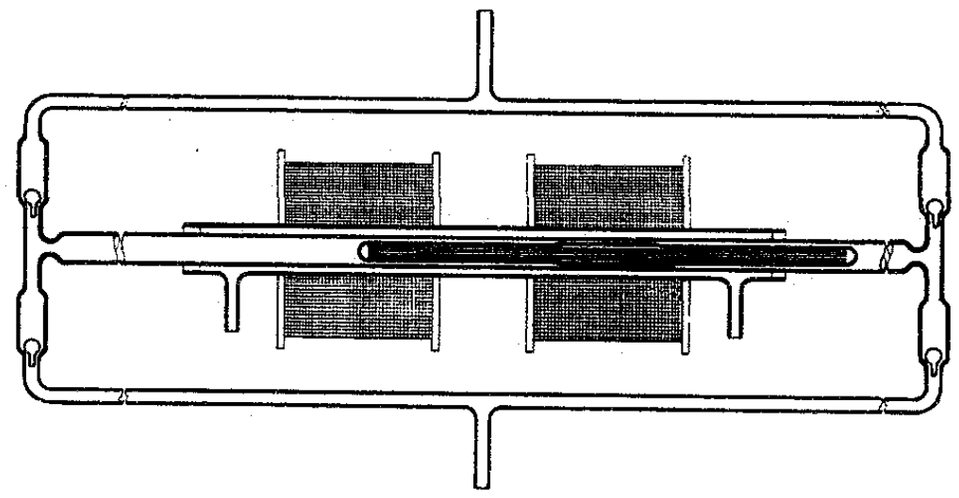


FIG. 1

diameter of 9 mm. The piston has a total length of 20 cm. fitting the barrel fairly snugly for about 10 cm. in the middle, and is packed with lengths of soft iron wire. The valves are very thin glass bulbs, unground, and seat in carefully made constrictions in 9 mm. tubing. The solenoids are alternately excited 78 times a minute by a commutator.

The pump forces dried air at atmospheric pressure against a head of 0.5 cm. of water at the rate of 55 litres per hour, using 2 amperes, against 18.5 cm. 12 litres per hour and has operated against 30 cm. The higher pressures of course require more current. Owing to the double action the flow of gas is practically continuous. The pump circulates dry gases in a closed system (containing a sulphuric acid bubbler) at all pressures down to as low as 11 mm.

Obviously a pump designed for circulating gases is not ideal for pumping liquids, but a duplicate pump, equipped with solid glass valves, circulates water at a rapid rate, and will raise it to a height of more than four feet. Doubtless this performance could be considerably improved by attention to the necessary details.

In the construction of this type of pump, all adjustments of solenoids, piston and length of barrel can be made before the valves are attached, which is a decided advantage.

* Contribution from the Chemical Laboratory, University of Toronto.

Although we have experienced no trouble with breakage ourselves, we recommend that the piston be stopped by gradually reducing the current.

As compared with other pumps that have been described[1] this pump appears to be more positive in its action and of easier construction. In addition it has a much greater capacity and can be readily adjusted to operate over a wide range of pressures.

[1] Porter, Bardwell and Lind: Ind. Eng. Chem., **18**, 1086 (1926).

SOCIÉTÉ DE CHIMIE INDUSTRIELLE
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ANNULÉ

GERMANIUM. XIX.[1] THE VAPOR PRESSURE OF GERMANIUM TETRABROMIDE[2]

BY F. M. BREWER AND L. M. DENNIS

Researches upon germanium dibromide which are described in a separate article involved the fractionation of a mixture of germanium bromoform and germanium tetrabromide. Of these two compounds, the tetrabromide had already been prepared and investigated,[3] but nothing was known about its vapor pressure-temperature curve apart from the melting point (26.1°) and the boiling point (185.9°) given by Dennis and Hance. As a guide to the fractionation, the vapor pressure curve was determined for temperatures between zero and the boiling point.

Preparation of Germanium Tetrabromide

A reflux condenser was sealed to the neck of a round flask of half-liter capacity, the top of the condenser being constricted so that the outlet was about three millimeters wide. An inlet tube to which a separatory funnel could be attached was also fused to the flask. Five grams of finely divided germanium was placed in the flask, and bromine in excess of the theoretical requirement for the formation of germanium tetrabromide was run in from the separatory funnel. The mixture was refluxed for four hours, the temperature of the heating bath being held at 60°. By means of a bath of this temperature and the restricted outlet, evaporation of the bromine was reduced to a minimum. When the germanium had been converted to the tetrabromide, most of the excess bromine was distilled off by heating on a steam bath. The residue was still colored by traces of bromine, which were removed by shaking the product with mercurous chloride. The germanium tetrabromide was then filtered and fractionally distilled. The fractionating column was sealed directly on to the neck of the distilling flask and was filled with glass beads. The main fraction distilled within a range of one degree, and was further purified by crystallization and filtration at about 15°. The melting point of the final product was 26° (uncorr.)

Apparatus

The principle of the apparatus used for determining the vapor pressure was identical with that described by Laubengayer and Corey.[4] Modifications were necessary in the construction, however, as germanium tetrabromide is a solid at ordinary temperatures. The sample bulb and fractionation bulb[5]

[1] Contribution from the Department of Chemistry, Cornell University.

[2] This article is based upon part of the thesis presented to the Faculty of the Graduate School of Cornell University by Frederick M. Brewer in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Winkler: J. prakt. Chem., 144, 193 (1887); Dennis and Hance; J. Am. Chem. Soc., **44**, 299, (1922).

[4] Laubengayer and Corey: J. Phys. Chem., **30**, 1045 (1926).

[5] These are marked *F* and *O* respectively in Fig. 2 of the article by Laubengayer and Corey.

of the original apparatus were discarded and a small distilling flask was attached at B, Fig. 1, to the limb of the vapor pressure tube R which was eventually to contain the sample. A vertical side-tube C was sealed into the lower wall of the connecting delivery tube, and this served the purpose of a fractionating bulb. The upper end of Q was attached to the main chain as shown in Figure 2 of the article cited.

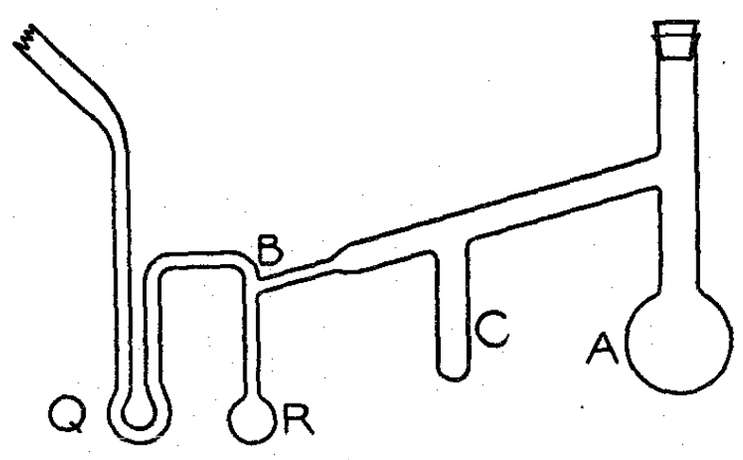


FIG. 1

Procedure

A small sample of carefully dried crystals of germanium tetrabromide was placed in the distilling flask A, which was then closed with a cork. The flask was immersed in liquid air and the whole apparatus was evacuated. The pressure in the apparatus was less than one millimeter of mercury. The sample was then melted and frozen three or four times at this reduced pressure, to liberate occluded gas. Preliminary runs showed that this precaution was very necessary, since it is difficult to remove the traces of hydrogen bromide resulting from slight hydrolysis by atmospheric moisture. This is unavoidable during the purification of the tetrabromide by freezing, and the transference of the sample to the distillation flask.

The sample was finally distilled into the vapor pressure bulb R, and was frozen by means of liquid air. The residue and the first fraction retained by the side tube C were frozen simultaneously, and the vapor pressure tube was sealed off at the junction of the delivery tube B. The small differential manometer was then established in Q after which the procedure followed the lines indicated by Laubengayer and Corey. In the preliminary experiments, the heating bath was one of sulphuric acid, but this was replaced for convenience of observation by a water bath for temperatures between zero and 90°, and by an oil bath for temperatures between 80° and the boiling point of germanium tetrabromide.

Even the removal of the hydrogen bromide did not prevent the formation at high temperatures of mercuric bromide, which came from the reduction of the germanium tetrabromide by the mercury of the manometer. The deposit which formed on the surface of the mercury, and on the walls of the manometer prevented accurate checking of the determinations during the cooling

of samples, as the mercury no longer moved freely in the manometer tube and the meniscus could not clearly be seen. These difficulties entered only at comparatively high temperatures while the observations are being made at increasing temperatures, and could be obviated to a great extent by keeping the external pressure a little in excess of the vapor pressure most of the time.

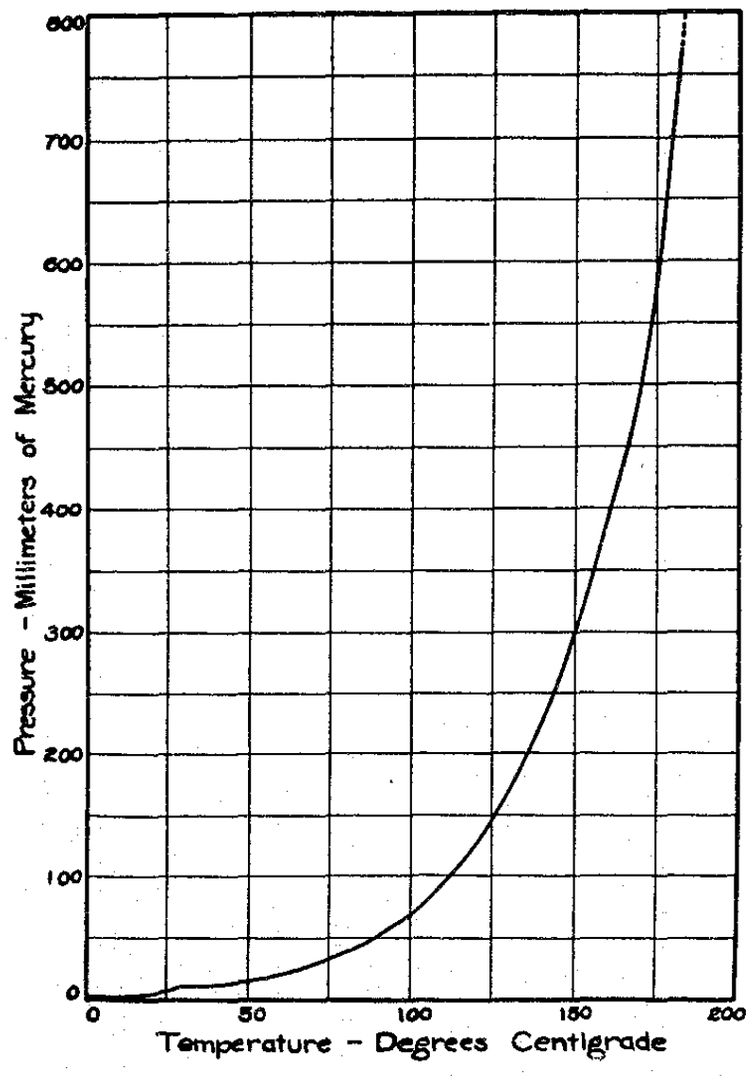


FIG. 2

The observed values for the vapor pressure were corrected for the vapor pressure of the mercury and mercuric bromide present. The necessary data were obtained from the tables of Landolt-Börnstein-Roth. The following additional corrections were also necessary:

(1) A calibration correction for the thermometer.

(2) An exposed stem correction for the thermometer.

(3) A brass scale correction for the barometer and manometer.

The calibration correction was determined for the thermometer by comparison at various temperatures with standardized Anschütz thermometers, and interpolation values were taken from the correction curve so obtained.

Exposed stem corrections were calculated for each reading. The formula used for the barometer scale correction was

$$B_o = .0001815 \left(1 - \frac{.000185 - .0000184}{1 + .0001815}\right) B$$

The curve plotted from the corrected temperatures and pressures observed in the two final determinations is given in Fig. 2. The two determi-

Vapor pressure of germanium tetrabromide. First determination.

Temp. °C. (corr.)	Press. (obs.) mm.	Corrections applied Scale mm.	Hg.	$HgBr^2$	Press. (corr.) mm.
4.45	1.6	—	—	—	1.6
18.35	3.2	—	—	—	3.2
23.05	4.1	—	—	—	4.1
27.85	4.1	—	—	—	4.1
32.70	5.1	—	—	—	5.1
37.60	7.6	—	—	—	7.6
45.60	10.2	—	—	—	10.2
47.65	11.3	—	—	—	11.3
57.84	17.1	—	—	—	17.1
68.10	24.1	−0.1	—	—	24.0
78.34	34.6	−0.1	−0.1	—	34.4
88.55	46.8	−0.1	−0.2	—	46.5
93.65	58.8	−0.2	−0.2	—	58.4
86.76	39.3	−0.1	−0.2	—	39.0
88.84	46.6	−0.1	−0.2	—	46.3
99.20	63.4	−0.2	−0.3	—	62.9
104.31	78.8	−0.3	−0.3	—	78.2
109.44	91.0	−0.3	−0.5	−0.2	90.0
114.53	109.4	−0.4	−0.6	−0.2	108.2
120.84	131.6	−0.4	−0.8	−0.3	130.1
124.66	149.6	−0.5	−0.9	−0.5	147.7
129.76	175.5	−0.6	−1.2	−0.8	172.9
134.89	202.2	−0.7	−1.5	−1.0	199.0
140.03	235.9	−0.8	−1.9	−1.3	231.9
145.45	271.8	−0.9	−2.3	−1.8	266.8
150.14	311.4	−1.0	−2.8	−2.5	305.1
155.33	361.8	−1.2	−3.4	−3.1	354.1
160.41	409.8	−1.3	−4.2	−4.0	400.8
165.55	467.5	−1.5	−5.0	−5.0	456.0
170.71	533.9	−1.7	−6.1	−6.5	519.6
175.10	604.8	−2.0	−7.2	−8.3	587.3
180.23	676.5	−2.2	−8.8	−10.5	655.0
182.27	701.4	−2.3	−9.4	−11.8	677.9
184.62	744.2	−2.4	−10.1	−13.4	718.3
185.34	758.5	−2.5	−10.4	−13.5	732.1
186.37	782.9	−2.6	−10.8	−14.2	755.3

nations agree entirely above 100°. Below 100° the second falls slightly below the first, but agrees better with the observed freezing point of germanium tetrabromide, 26.1°. The discrepancy between the two curves was probably due to uneven heating of the water bath in the first determination, and the difficulty of adjusting the differential manometer for the very slight changes of pressure recorded near the freezing point. The boiling point derived from the curve plotted in accordance with these determinations falls at 186.5° which is in good agreement with the value obtained by Dennis and Hance.

Vapor pressure of germanium tetrabromide. Second determination.

Temp. °C. (corr.)	Press. (obs.) mm.	Corrections applied			Press. (corr.) mm.
		Scale mm.	Hg.	$HgBr^2$	
18.35	3.6	—	—	—	3.6
27.85	6.9	—	—	—	6.9
37.60	8.5	—	—	—	8.5
47.65	10.4	—	—	—	10.4
57.84	14.7	—	—	—	14.7
62.95	18.9	—	—	—	18.9
68.10	22.1	−0.1	—	—	22.0
73.20	26.1	−0.1	—	—	26.0
78.34	31.3	−0.1	−0.1	—	31.1
83.45	39.6	−0.1	−0.1	—	39.4
88.55	44.0	−0.1	−0.2	—	43.7
93.65	52.9	−0.2	−0.2	—	52.5
100.26	66.5	−0.2	−0.3	—	66.0
103.82	78.4	−0.2	−0.3	—	77.9
108.90	87.7	−0.3	−0.4	−0.2	86.8
113.94	106.3	−0.3	−0.6	−0.2	105.2
119.00	124.6	−0.4	−0.7	−0.3	123.2
124.18	145.7	−0.5	−0.9	−0.5	143.8
129.13	169.4	−0.6	−1.2	−0.8	166.8
134.23	197.3	−0.7	−1.4	−1.0	194.2
139.33	228.2	−0.8	−1.8	−1.3	224.3
144.43	266.6	−0.9	−2.2	−1.8	261.7
149.50	306.3	−1.0	−2.8	−2.5	300.0
154.60	354.3	−1.1	−3.3	−3.1	346.8
159.71	402.1	−1.3	−4.1	−4.0	392.7
164.88	460.5	−1.5	−5.0	−5.0	449.0
170.00	522.3	−1.7	−6.1	−6.5	508.0
175.15	594.9	−1.9	−7.3	−8.3	577.4
180.39	671.3	−2.2	−8.8	−10.5	649.8

Summary

The vapor pressure of germanium tetrabromide has been determined for the temperature range 0° to the boiling point. The value of the boiling point of germanium tetrabromide obtained from this determination is 186.5°.

Ithaca, New York.

NEW BOOKS

Introduction to Physiological Chemistry. *By. Meyer Bodansky. 23 × 15 cm; pp. vii + 440. New York: John Wiley and Sons, 1927. Price: $4.00.* "In aiding the student to correlate physiological chemistry with allied sciences and to define its scope, a textbook fulfills a very useful purpose. A small book, if it is sufficiently coherent and comprehensive, is likely to serve this purpose better than a large one, valuable as the latter may be as a reference. It was this idea that stimulated the author to write the present book. He has aimed to make it brief enough for use as an introductory volume and yet to give it sufficient scope to cover the field comprehensively. Laboratory methods and the description of tests have been omitted intentionally, since they are to be found in laboratory manuals devoted to the subject. The main aspects to physiological chemistry have been developed in relation to recent advances in the science. It is hoped that in this way the student will be afforded not only a knowledge of fundamental principles but also a realization of the developmental state of the subject.

"It is obvious that a certain amount of condensation has been necessary, but the author hopes that he has not condensed the material at the expense of vital information. Wherever he has felt that collateral reading would be desirable, he has referred the student to easily accessible sources, such as journal articles, reviews, monographs, and other works. The student who enters upon the study of physiological chemistry is, strictly speaking, not a beginner. He is not unfamiliar with the principles of inorganic and organic chemistry, and in many cases he has received some training in physico-chemical concepts. He has therefore attained sufficient maturity to profit by collateral reading," p. 5.

The chapters are entitled: introduction; the carbohydrates; the fats; the proteins; digestion and the chemistry of enzyme action; absorption and intestinal putrefaction; the blood and lymph; physiological oxidations; intermediary metabolism of carbohydrates; intermediary metabolism of fat; intermediary metabolism of protein (2); excretion—the urine; internal secretions; animal calorimetry; nutrition.

"Macullum and, somewhat earlier, the German physiologist, Bunge, have suggested that the high content of sodium chloride in the blood of vertebrates may be an inheritance from our remote ancestors who lived in the sea. Supposing that these animals took to the land after the development of a closed circulatory system, it might follow that the composition of the sea, as it was at that time, has persisted in their blood to the present day. How, then, are we to account for the divergence in potassium and magnesium? It has been suggested that since the Cambrian period less potassium has been supplied to the sea than prior to the time, because so much of this element has been required by plant life, which has been more profuse since the Cambrian era. On the other hand, the magnesium content of the ocean and the proportion of magnesium to sodium have been steadily increasing since pre-Cambrian time, the concentration found at present in the higher animals corresponding presumably to the low magnesium content of the sea at the time the animals in question acquired a terrestial habitat. The calcium content has been increasing but slowly, owing perhaps to the utilization of calcium in the building of corals and the bones and shells of other marine organisms. To sum up, it may be supposed that the blood serum of mammals resembles, except for the difference in its magnesium content, diluted sea water of our own day," p. 7.

"While the possibility of direct linkage between carbon atoms of amino acids (C-C) and of ether-like linkages (C-O-C) is not excluded, the following considerations support the view that in the protein molecule the amino acids are linked together almost entirely through the amino group of one amino acid and the carboxyl group of another, forming long chains of amino acids. In the first place, the protein molecule has few free amino and carboxyl groups, these increasing in number when the protein molecule is disintegrated by enzymatic or acid hydrolysis. Secondly, a number of polypeptide compounds have been synthesized in which there is but one free carboxyl group and one free amino group and in

which the individual amino acids are joined together by means of the so-called peptide (O=C−NH−) binding," p. 70.

"A distinction is frequently made between the enzymes and the inorganic catalysts on the basis of their relative specificity. Colloidal platinum catalyzes a variety of reactions, such as the decomposition of hydrogen peroxide, the hydrolysis of esters of the simple alcohols, and the formation of nitric acid and sulfuric acid. In other words, platinum as a catalyst is not limited to a single reaction. Hydrogen ions likewise catalyze a large number of hydrolytic reactions. On the other hand, enzymes are more or less limited to a single reaction. For example, catalase decomposes hydrogen peroxide and has no effect upon any other reaction. The velocity of the hydrolysis of urea is increased by the enzyme urease. Invertase acts on sucrose but not on maltose or lactose. Pepsin digests proteins but has no effect on carbohydrates or fats.

"However, it must be emphasized that this distinction in specificity is not as sharply drawn as it appears. Inorganic catalysts do show some degree of specificity. Tungstic acid aids in the oxidation of hydriodic acid by hydrogen peroxide, but does not accelerate the oxidation of hydriodic acid by a persulfate. In the case of iron salts, the oxidation of potassium iodide by a persulfate is catalyzed, whereas no effect is produced on the oxidation of sulfurous acid by the same persulfate. Even platinum black exhibits certain peculiarities in behavior toward esters. Hydrolysis of the esters of simple alcohols is accelerated, whereas the effect produced on the glycerol esters is hardly appreciable. Taylor points out that acids, though very active in many hydrolytic reactions, have no effect on the conversion of adenine and guanine into xanthine and hypoxanthine," p. 94.

"A very interesting experiment and one that may have some bearing on the problem of acid formation is that of T. B. Osborne. He dissolved edestin in sodium chloride solution and later precipitated it with a stream of carbon dioxide. The precipitate contained edestin in combination with hydrochloric acid, whereas the solution contained $NaHCO_3$. Obviously, in the presence of the protein edestin the reaction represented by the equation $NaCl + H_2CO_3 = NaHCO_3 + HCl$ was facilitated.

"Behavior similar to that exhibited by edestin can be demonstrated with red blood corpuscles. If these are washed in isotonic solutions of sodium chloride until the washings are neutral, then suspended in neutral sodium chloride solution and treated with a stream of carbon dioxide, it is found that the solution becomes alkaline and the corpuscles richer in chlorine. From these observations, Robertson infers that the secretion of an acid juice depends upon the existence in the secreting cells of a protein that is capable of decomposing sodium chloride in the presence of carbon dioxide, the appearance of the free hydrochloric acid in the secretion being attributable to the colloidal, indiffusible character of the protein base. The validity of this suggestion remains to be determined by further study," p. 118.

"Beginning with the alimentary system, the problem of cell permeability arises in many forms. Why, for example, does practically no absorption, even of water, occur in the stomach, while taking place with the greatest ease in the small intestine? Why, in the latter, are some substances absorbed much more rapidly than others; for example, NaCl more rapidly than Na_2SO4, dextrose more rapidly than sucrose, etc.? Why does NaCl readily enter the blood stream from a solution introduced into the gut but pass with difficulty in the reverse direction? Does the wall of the intestine show evidence of a one-sided permeability to water? What are the means by which water is taken up, not merely from hypotonic, but from isotonic and hypertonic solutions as well? What is the mechanism of normal absorption of the different kinds of digested food materials?" p. 134.

"Proteins, therefore, are foods when absorbed in the usual way as amino acids, and poisons when introduced directly into the blood. One of the most violent poisons known is ricin, the protein of the castor bean. The injection of a protein that is foreign to the tissues of an animal results in the excretion of most of it in the urine. If the injection is repeated a few days later, no ill effects ensue. Continued injection of a given protein at short intervals establishes an immunity for that protein, due, it is believed, to the formation of a precipitin, in the presence of which the foreign protein is precipitated. If, however, the second injection is administered several weeks after the first, severe shock is induced. This

phenomenon is termed *anaphylaxis* and has among its symptoms a marked fall in blood pressure and a reduction in the coagulability of the blood. According to some investigators, anaphylactic shock and peptone shock are essentially the same, the former being due to the development in the sensitized animal of an enzyme capable of converting the foreign protein in question into proteoses and peptones. "Serium-sickness" frequently occurs in individuals sensitized against horse-serum proteins, and develops after the injection of antitoxins, such as diphtheria antitoxin. Under these conditions, typical anaphylactic shock occur and may terminate fatally.

"Idiosyncrasies toward food proteins are likewise known. Certain individuals are unable to tolerate egg or milk proteins. Others, after eating strawberries or sea food, develop skin eruptions, asthma, and other anaphylactic reactions. These idiosyncrasies are attributed to the absorption of native or unchanged proteins found in these foods. Exceedingly small amounts (less than 1 milligram) are frequently sufficient to produce typical intoxications.

"Occasionally, therefore, unchanged protein may be absorbed from the intestine. When this happens, the protein behaves as a foreign substance, or, where the individual has been previously sensitized to that protein, it behaves as a poison. Ordinarily, however, protein is absorbed almost entirely in the form of amino acids," p. 139.

"Heidenhain has shown that sodium chloride solutions of osmotic pressure greater than or equal to the osmotic pressure of the blood, when injected into an isolated loop of the intestine, are absorbed indifferently. According to the laws of osmosis, no water should pass from the intestine into the blood in the first case, and in the second, no absorption of any kind should take place.

"Cohnheim studied the interchange of substances between the intestine and the circulating fluid in dead animals by pumping through the blood vessels a solution of sodium chloride (0.94 percent). A sugar solution was placed in an isolated loop of the intestine, with the result that interchange of material occurred in both directions, sugar passing into the circulating fluid and sodium chloride into the intestine. There was no diminution in the volume of the intestinal contents. These observations have led many to the conclusion that absorption is due to some specific activity of the living epithelium. This, however, does not bring us any closer to the solution of the problem. It should be borne in mind that the circulating fluid in Cohnheim's experiment could not be expected to have the properties of blood. On the basis of what has been said in regard to Donnan's theory of membrane equilibrium (page 24), the blood proteins must play an important rôle in absorption by determining the distribution of electrolytes on the two sides of the intestinal membrane. The entire problem of intestinal absorption is a difficult one. The literature pertaining to the subject has been reviewed by Goldschmidt," p. 140.

"It is well known that the hemoglobins of no two animals yield exactly the same spectra. However, when different hemoglobins are treated with alkali and reducing agents, the product obtained yields, as far as we know, spectra which are identical. It has therefore been assumed that the hemochromogen part of hemoglobin, *i. e.*, the portion of the molecule responsible for the identical spectra, is the same for all hemoglobins, that it is a non-protein nucleus, and, moreover, that the differences in the spectra of the hemoglobins are to be attributed to differences in the proteins attached to this nucleus.

"Barcroft has questioned the truth of this hypothesis, basing his views on the recent work of Anson and Mirsky These workers have shown that hemochromogen, *i. e.*, the substance that gives the "hemochromogen spectrum," is not a protein-free body, but a substance similar in structure to hemoglobin, but of a simpler nature. Hematin, or the oxide of hemochromogen, is likewise a conjugated protein.

"Keeping the new significance of hemochromogen in mind, we may now proceed to the second consideration, namely, that when hemochromogen and hematin are broken down so that the protein moiety is removed, two bodies are obtained; these are "reduced hem" and "hem" respectively. When hemin is treated with NaOH in the presence of a reducing agent, reduced hem is obtained; in the presence of oxygen, hem is obtained. Accordingly, $C_{34}H_{36}N_4FeO_5$, is hem. Its existence as the free base is hypothetical.

"Barcroft and his co-workers then point out that hemoglobin may be synthesized by starting from hemin, which is the chloride of the hypothetical base, hem. By the addition of sodium hydroxide the base is liberated. If it is treated at this point with a reducing agent, a body is obtained which gives a spectrum that is different from that of hemochromogen as we know it. If globin is added to hem, a product is obtained which is still not the substance that gives the "hemochromogen spectrum." The hem-globin body, thus formed, Barcroft, following the suggestion of Anson and Mirsky, calls α-hemochromogen. However, on the addition of globin to this compound, we obtain the substance giving the "hemochromogen spectrum." It is called β-hemochromogen. That hemoglobin is closely related to this compound is obvious from the fact that β-hemochromogen is transformed into reduced hemoglobin by the mere adjustment of the hydrogen-ion concentration. In passing from hem to hemoglobin, we are therefore confronted with a series of four different spectra:

Hem
↓
α-Hemochromogen
↓
β-Hemochromogen
↓
Hemoglobin

"It now becomes possible to offer an explanation of the fact that the hemochromogens of all mammalian bloods give bands of identical wave length. As long as the protein body is a globin, the spectral bands of the hemochromogens are in a constsnt position. The actual difference between hemoglobin and hemochromogen cannot be stated as yet. Hemoglobin may be a condensation product of hemochromogen. The position of the spectral bands alters with the nature of the nitrogenous body which may be joined to hem, thus indicating the possibility that, in nature, hemoglobin is but a special case of a large series of compounds of the same general type. Thus we may have or we may prepare ammonia-hemochromogen, hydrazine-hemochromogen, pyridine-hemochromogen, glycine-hemochromogen, albumin-hemochromogen, etc.," p. 161.

"The maintenance of the acid-base of the blood is not dependent upon any one buffer pair, but rather upon the total effect of several such pairs. The advantage of such an arrangement in providing security against acidosis or alkalosis may be likened to the advantage of having five guards on duty instead of one. It is obviously unsafe to leave a single individual to safeguard a treasure or to hold and defend a mountain pass against an enemy. No matter how well-armed he may be, he is always in great danger of being overcome. Five guards strategically placed would constitute a much more solid defense. If one or two of the guards were overcome, there would still be a few left to hold the enemy back for a time, perhaps even until help arrived. This analogy is quite apropos if we suppose the enemy to be H or OH ions, and the mountain pass the outer limits of the normal pH range of the blood. Of course, all five guards in our analogy might be overcome. Translated into terms of acid-base balance, this is what happens when coma or tetany develops."

"The distribution of electrolytes in the blood, including the transfer of chlorine and hydrogen ions between the plasma and corpuscles, can be explained on the basis of Donnan's theory of membrane equilibrium, by assuming that the membrane of the red cell is the semi-permeable membrane which separates the plasma from the fluid in the corpuscles. This membrane, as we have seen, is impermeable to cations and proteins but is permeable to H ions, H_2CO_3 and anions (Cl, SO_4 and PO_4). Electrolytes that are present on either side of the membrane will tend to distribute themselves equally on the two sides. This tendency will be opposed, however, by the attractive forces of the non-diffusible ions, with the result that when equilibrium is reached there will be an uneven distribution of ions on the two sides of the membrane," p. 174.

"We shall now consider briefly some of the physiological properties of glutathione. In his first paper, Hopkins pointed out certain relations in the behavior of fresh tissues toward meth-

ylene blue and glutathione. Fresh tissues, as is well known, reduce methylene blue. This dye is likewise reduced by the reduced form of glutathione. However, tissues are capable of reducing the oxidized form of glutathione. From these observations, it is to be concluded that the reduction potential of tissues is greater than that of glutathione, which in turn has a greater reduction potential than methylene blue. These relations are not always fixed, but, according to Hopkins' first experiments, are closely dependent on the hydrogen-ion concentration of the medium. In any event, at a pH of 7.4, Hopkins found the rate of reduction of methylene blue by washed tissues to be greatly accelerated upon the addition of small amounts of the oxidized glutathione.

"The explanation lies in the fact that the S—S group of the oxidized dipeptide acts first as a hydrogen acceptor. The hydrogen taken up is then transferred to the methylene blue. It would appear, therefore, that the two reactions, namely the transfer of hydrogen to the dipeptide and its subsequent transfer to the methylene blue, together run faster than the single reaction involving the direct transfer of hydrogen from the tissues to the dye. Of course, some other hydrogen acceptor can take the place of the methylene blue. In physiological oxidations, we must therefore consider the relation of glutathione to oxygen, the most available of hydrogen acceptors. The changes which glutathione undergoes in oxidation may be represented as follows:

$$2\ G.SH + O_2 = G.S.S.G. + H_2O_2$$
$$G.S.S.G. + H_2 = 2\ G.S.H.$$

"These equations need but little explanation. They represent glutathione in the position of a middleman, removing hydrogen from the tissues, or more properly from the metabolites, and passing it on to the oxygen. The oxygen peroxide is formed as a by-product and is perhaps prevented from accumulating by catalase, which, according to this scheme, assumes a definite function," p. 199.

"Mention has been made of the relation of iron to the oxidation of glutathione. This is, however, but one example of the part which iron plays in physiological oxidations, according to Warburg and his followers. Warburg believes that in respiring cells there is a cycle in which molecular oxygen reacts with bivalent iron, with the result that iron in a higher state of oxidation is formed. The oxidized iron is then supposed to react with organic substances, being thus reduced to bivalent iron, whereas the organic material is, at the same time, oxidized. Then the cycle is repeated.

"In support of this view, Warburg presents abundant evidence. It can be shown, for example, that the oxidation of cysteine to cystine is accelerated by iron salts; that, in fact, no auto-oxidation of cystine occurs when iron is entirely absent. Working with Meyerhof, Warburg has shown that iron controls the respiration or oxygen consumption of unfertilized, cytolyzed sea urchin eggs. In their experiments, these investigators determined the iron content as well as the oxygen consumption of the eggs, and, from these data, calculated the reactivity of the iron by dividing the oxygen consumed by the iron content. The eggs were then dissolved; 1/100 mg. of iron was added to 1 g. of the egg substance and the increase in oxygen utilization determined. It was found that the iron originally present in the intact egg had the same effect as the iron that was added. In both cases, each milligram of iron aided in the taking up of the same amount of oxygen per hour, namely, 7,000 cmm.

"Thunberg has shown that lecithin is readily oxidized in the presence of iron. This observation may be correlated with that of Warburg who found that the oxidation of linolenic acid is influenced similarly by iron. Moreover, Warburg found that the active material in the sea urchin eggs are lipoid in character. He was able to show that, upon the addition of iron, the extracted lipoids consumed an amount of oxygen equivalent to the oxygen consumption of a corresponding amount of egg substance.

"In order to have a direct bearing on cell oxidations, this discussion will be limited to the ability of iron to react with molecular oxygen, and will not touch upon its ability to react with oxygen in an activated form, as in ozone, hydrogen peroxide, or quinone. Free ferrous ions do not react with molecular oxygen to any appreciable extent, nor do they act as oxygen transferers. Warburg states that iron, in order to act catalytically, must be

present in some specific and as yet unknown combination. He has succeeded in demonstrating oxidations, closely akin to cell oxidation, in relatively simple systems. From pure hemin he has prepared charcoal which, when shaken in aqueous solutions of amino acids, caused chemical changes resembling reactions of metabolism. This occurred at body temperature and in solutions that were near neutrality. Thus, leucine yielded ammonia, carbon dioxide, and valeric acid. From cystine were formed ammonia, carbon dioxide, and sulfuric acid, in addition to some undetermined products of incomplete combustion," p. 200.

"It is important to bear in mind that not all the fat in the body has the same physiological significance. An apparently clear-cut and sound distinction has been made by a number of workers (Mayer, Schaeffer, Terroine and others) between the so-called *élément constant and élément variable.* The tissues of animals that have starved to death still contain a certain amount of fat, which seems to be fairly constant for any given species. In the mouse, for example, about 23 percent of the dry weight of the animal consists of fatty acids, whereas in the chicken the fatty acids constitute about 25 percent of the dry weight. It is believed that a certain amount of fat is an essential component of protoplasm, and that this cannot be reduced without causing death. This is the *élément constant.* On the other hand, the reserve fat is variable in amount, depending on the state of nutrition and other factors. The fatty acids in reserve or storage fat are present in combination with glycerol as neutral fat. Such fat, because it varies in amount, has been called by the group of workers mentioned above, the *élément variable.*

"It appears that the kidney, spleen, lung, and heart contain no *élément variable* but only the *élément constant.* This is demonstrated by comparing the composition of these organs in overfed, normal, and starved anaimals. Leathes cites data for the kidney, in which 11.1, 11.9, and 13.4 percent of fatty acids were found in overfed, normally fed, and starved animals, respectively. If anything, these data, instead of showing that fat is stored on a high-fat diet, indicate that there is a greater migration of fat to this organ during starvation than normally. In muscle, the figures obtained in the conditions just mentioned were 17.6, 11.3, and 4.6 percent, showing unmistakably the possibility of the storage of fat in muscle tissue. Finally, the values given for the liver are 12.9, 10.5, and 11.3 percent. Thus, the liver does not seem to play as important a part in fat storage as is often supposed. Occasionally, the amount of fat in the liver may increase considerably, usually as a result of sudden fat mobilization, but even then the storage of fat in this organ is believed to be transitory," p. 244.

"The interrelationship between carbohydrate and fat metabolism is indicated by the oft-repeated statement that "fats burn in the flame of carbohydrate," and by the statement of Macleod that "if the carbohydrate fires do not burn briskly enough, the fat is incompletely consumed; it smokes, as it were, and the smoke is represented in metabolism by the ketones and derived acids," p. 250.

"Obesity is usually the result of overnutrition, lack of exercise, or both. It is a matter of common observance, however, that certain individuals increase in weight despite an apparently moderate diet, while others remain thin in spite of all efforts to gain weight by overeating. Then there is the average individual who makes no conscious attempt to control his diet but whose weight remains fairly constant over a period of many years. Obesity is very common and appears to be hereditary. The view which is gaining headway at present associates obesity with derangements of the endocrine organs. Diseases of the hypophysis, castration, the menopause, myxedema, and other physiological and pathological disturbances are usually, but not invariably, accompanied by the deposition of an abnormal amount of fat. A distinction has been pointed out by Grafe between so-called exogenous obesity and the endogenous or constitutional type, the former being due to laziness and overnutrition, whereas the latter is believed to be in some way associated with endocrine disturbance," p. 253.

"The physiological importance of inorganic constituents has been brought out in numerous other connections and does not require further emphasis at this point. The extraordinary influence of the mineral elements in nutrition, although it has been appreciated to some degree for many years, was not clearly understood or quantitatively studied

until quite recently. In a long series of experiments which began not quite twenty years ago, Hart, McCollum and Steenbock studied the growth and reproduction of cattle upon restricted diets of various grains. These investigators divided their experimental animals into four groups. All the animals received approximately the same amount of sodium chloride. The ration which was fed to one group was derived solely from the wheat plant and consisted of wheat straw, wheat gluten, and the entire wheat grain. The second group received a ration derived from the corn plant. The third group fed on the products of the oat plant. The fourth group of animals received a ration consisting of a mixture of wheat, corn, and oats in about equal proportions. It was discovered that the nutritive condition of the corn-fed animals was much better than that of any of the remaining groups. The wheat-fed cattle fared worst. The corn-fed animals gave birth to normal young and reared them. The offspring of the wheat-fed cows were not carried to full term, and those that were not born dead usually died several days after birth. The behavior of the animals in the remaining two groups was intermediate between the two extremes observed in the corn-rationed and wheat-rationed groups. The untoward manifestations noted in the wheat-fed animals, as well as in those maintained exclusively on oats, were shown to be due largely to a deficiency in mineral constituents, chiefly calcium," p. 362.

"Experience in the rearing of lions and other carnivorous animals in several zoological gardens has brought out very strikingly the importance of calcium in nutrition. It is now fully understood that the difficulty formerly encountered in bringing up lions in captivity was due largely to the fact that the diet, after weaning was inadequate, consisting as it did almost entirely of raw meat. Even lions, when they are young, find it difficult to chew the large bones which are usually thrown to them. As a result, the young lions kept on this diet developed a severe form of rickets and succumbed. However, when the diet was supplemented by the addition of calcium-rich food, such as milk and crushed bones, and by the addition of cod-liver oil (the latter contains the anti-rachitic vitamin), the animals grew normally and those which had previously developed rickets were frequently cured," p. 368.

"The problem of iron metabolism has not been studied as energetically as is warranted by its importance. Whipple and his associates have, however, contributed much to our knowledge of the relation of diet to blood regeneration in anemic conditions. They have shown that meat, particularly that of organs (heart, liver), is especially beneficial in hemoglobin and red-cell formation. That this is due to the relatively high concentration of iron in these substances is borne out by the analyses of Forbes and Swift. These workers have found that beef contains twice as much iron as do potatoes; two and a half times as much as white flour and corn meal; and eight times as much as apples. Certain vegetables (peas, beans, lentils, spinach, graham flour, oatmeal, and shredded wheat), contain more iron than does beef. The richest source of iron is to be found, however, in organ meats or "extra carcass parts." Beef heart and brain contain about twice as much iron as do beef and veal. Beef liver is twice as rich in iron as is beef heart. The iron content of the beef spleen exceeds that of the liver by 50 percent. These observations are of the utmost importance and suggest that the utilization of these parts in human nutrition should be given serious consideration," p. 370.

The author still clings to Loeb's point of view. "The formerly accepted view that the addition of acids and alkalies to proteins results in the formation of adsorption compounds must give way to the chemical viewpoint postulated by Loeb and supported by his quantitative proof that proteins combine with acids and bases in stoichio-metric proportions," p. 81. *Wilder D. Bancroft*

Treatise on Sedimentation. *By William H. Twenhofel. 24 × 16 cm; pp. xxv + 661. Baltimore: The Williams and Wilkins Company, 1926. Price: $7.50.* The chapters are entitled: introduction; sources and production of sediments; the transportation, deposition, diagenesis, and lithification of sediments; important conditions modifying sedimentary processes; sediments and organisms; products of sedimentation; structures, textures, and colors of sediments; environments or realms of sedimentation; field and laboratory studies of sediments.

"Sedimentation includes that portion of the metamorphic cycle from the separation of the particles from the parent rock, no matter what its origin or constitution, to and including their consolidation into another rock. Sedimentation, thus, involves a consideration of the sources from which the sediments are derived; the methods of transportation from the places of origin to those of deposition; the methods, agents, and environments of deposition; the chemical and other changes taking place in the sediments from the times of their production to their ultimate consolidation; the climatic and other environmental conditions prevailing at the places of origin, over the regions through which transportation takes place, and in the places of deposition; the structures developed in connection with deposition and consolidation; and the horizontal and vertical variations of the sediments.

"Sediments are defined as the deposits of solid material (or material in transportation which may be thus deposited) made from a mobile medium on the surface or in the outer crust of the earth under conditions of temperature normal to the surface and under the influence of gravity. Some transportation is involved, but it may range from essentially mere detachment of the particles from the parent rock to many miles. It must have been sufficiently great to have destroyed textures and structures of the parent rock except as these are preserved in the particles. The solid matter may be of organic or inorganic origin. The condition of temperature normal to the surface excludes from sediments the precipitates from magmas, but includes those from water, although it is recognized that the processes involves in precipitation are much the same. The medium may be air, water, or ice. The recognition of gravity as a factor in deposition permits the inclusion of such deposits as talus accumulations and the material mantling the surface. Not limiting the place of deposition to the surface of the earth permits the inclusion of the deposits of caves and smaller cavities and the cementing material which is brought in by waters of surface temperatures, but excludes the deposits which are made by highly heated waters, although it is granted that these are not sharply separated from those made by waters of lower temperatures. The materials ejected from volcanoes are considered if their temperatures at the times of deposition are sufficiently low as not to be an important factor in consolidation. Under all conditions the type and extent of a sediment which may be deposited is a consequence of the environment, from which it follows that the various components of the environment are reflected in the sediments therein formed," p. XXIII.

"As temperatures over most parts of the earth surface vary, expansion and contraction are often repeated, and ultimately the cohesion of the minerals for one another disappears and the rock falls apart into its constituent minerals. This may be defined as granular or mineral disintegration. As most minerals have different coefficients of expansion parallel to unlike axes and as there is little uniformity of orientation of crystal axes in a rock, the effects are the same for rocks composed of a single or many minerals. Thus, Ordovician limestones in Northern Kentucky which had been exposed on the surface for perhaps a score of years became loosely interlocked crystals of calcite, and Trenton dolomites near Blue Mounds, Wisconsin, have fallen apart into separate rhombohedrons of dolomite," p. 4.

"Under rock disintegration it was noted that the effects are largely confined to a thin zone near the surface, and that the process is favored by exposure. Rock decomposition, on the other hand, may take place to depths as great as the surface waters extend. Thus, in the District of Columbia it is stated that the granite rocks are decayed to a depth of 80 feet so as to be easily removed with pick and shovel, while Spencer states that the rock near Atlanta, Georgia, is locally decayed to a depth of 95 feet, and in northwestern Georgia the depth of decay of limestones reaches to 200 feet. In Brazil Derby has noted the decay of shales to a depth of 394 feet, and in South Africa in the Transvaal, the granite of the Dakaap goldfields is decomposed to a depth of 200 feet," p. 13.

"Deep sea deposits contain small particles which are referred to a meteoric origin. These drop over the entire earth, but are generally masked on the land and in shallow water by the abundance of other sediments. It is estimated that from fifteen to twenty million enter the atmosphere daily, contributing an annual addition to the earth's sediments of from 5000 to 7000 tons, which would make a deposit on the sea bottom of 1 foot in about fifty billion years," p. 22.

"Mountain regions rising above the timber line lose all their fine material to the winds. Regions of high latitude free of vegetation or snaw have all fine material blown away. Cape Sand Top on the east end of Anticosti Island is a barren area over limestone which has been greatly shattered by frost action and from which the winds have removed all the fine material. The surfaces of glaciers and the deposits made where they melt yield volumes of dust, and on sea and lake shores large quantities of sand and small shells are carried inland for long distances. Volcanoes are unique in that the material contributed by them is shot into the higher currents of the atmosphere independent of the atmosphere itself, while material of cosmic origin enters the atmosphere from above. The quantity of the latter, however, is so small that its presence is not appreciable in atmospheric deposits. Animals on dry lands raise great volumes of dust by stirring it up with their hoofs, and Passarge expressed the opinion that the chief agents of past erosion of such lands were the great herds of vertebrates there found and that to them were due the gently inclined plains free from river furrowing. Man through his different industries and activities is daily providing the atmosphere with enormous volumes of material, and his coal dust will be found in the geologic future in many deposits," p. 51.

"Lakes in mountain regions have shores of considerable relief, so that a variety of environments is close to water, and hence there is an excellent opportunity for a mixed association of excellently preserved material. This could be differentiated from the deposits of small bodies of water with low shores on the basis of the mixed association and from others of mixed association on the bases of the excellent preservation and the absence of many resistant structures. As many mountain ranges have volcanoes, an ash shower may cover the lake and bring floating leaves to the bottom in large quantity and this lead to an excellent preservation of all the floating matter carried down, as exemplified by the leaves and insects exquisitely preserved in the Florissant shales of Colorado," p. 124.

"The shapes developed by artificial abrasion of angular fragments in a tumbling mill and those developed by abrasion in natural streams of relatively high gradient and moderate load in a humid region are closely similar. In the relative rates of wear on corners and sides, in the convexities developed on the corners and sides, and in the details of the approach toward spherical forms, there seems to be little difference between the two methods. In streams of this sort, universally oriented tumbling and bumping seem to be dominant, and sliding, lateral rolling, or any other special sort of motion seem to be quite subordinate," p. 156.

"The deposition of cement around and between the grains of a sand converts it into a sandstone. The three principal cementing materials are quartz, limonite, and calcite, important in the order named. Other cements are opal, chalcedony, magnetite, hematite, and magnesium and other carbonates. There is great variation in the extent of cementation. Some sands are so slightly cemented that they may be pulverized in the hand, while others have been converted into quartzite. Quartz cement is commonly deposited in optical continuity with the crystal structure of the sand grains, so that the new particles have regular crystal outlines. The rock may or may not be firm," p. 173.

"The green muds differ from the green sands chiefly in the association of quartz sand with the latter. The chief distinction from the blue and gray muds is the presence of glauconite. This appears to form as a consequence of certain relations between the quantity of organic matter in the sediments and the other materials. If there is an excess of organic matter, blue or black mud appears to result, in which hydrogen sulphide develops with the ultimate formation of ferrous sulphide. If the organic matter falls below a certain, not yet determined, percentage, ferrous sulphide does not form, but instead ferrous sulphate from which the potassium silicate of iron or glauconite results. If sediments contain a large quantity of ferric hydrate or are composed of river detritus which accumulated at a rapid rate, glauconite does not develop and hence these muds are not green," p. 197.

"Most bentonite is believed to develop through the alteration of volcanic ash, a view first advanced by Hewett. The facts on which the view is based are the uniform composition and thickness over a great area, the mineral associations and volcanic matter which are present, and the difficulty of accounting for its origin by other sedimentary processes.

The origin as presented by Wherry applies to the Cretaceous bentonites of the northwest and is to the effect that ash settled in the Cretaceous sea. As it fell in the water, the heavier minerals sank to the bottom first, so that they are most abundant in the basal portion of each bed; and as they were not exposed to atmospheric conditions, they remained essentially in fresh condition. The volcanic glass composing the ash is supposed to have been porous and to have contained various gases, so that a kind of autometamorphism took place with the clay-like mineral composing bentonite as the product. Wherry suggests a mica-andesite ash for the bentonite south of the Black Hills, while Larsen states that the Tennessee bentonite is a decomposed rhyolite ash which "altered immediately following eruption into a material somewhat akin to leverrierite." In every case the deposition must have been very rapid; otherwise considerable proportions of sediment of other origin could not have failed to have become incorporated," p. 208.

"Limestones are composed either of calcite or dolomite. Those which are dominantly composed of the former are the calcite limestones. These are considered under the heading of limestone. If the dominant mineral is dolomite, the rocks are dolomites or dolomite limestones. Many calcite limestones contain more or less dolomite, and many contain some magnesium carbonate not in the form of dolomite, but in isomorphous mixture with the calcite. Where the quantity is important, the rock may be called either a dolomite or magnesium limestone, depending on the form in which the magnesium carbonate occurs," p. 123.

"So far as studied the shells composed of aragonite are almost completely non-magnesium, and the small quantity they contain may be due to impurity or alteration. On the other hand, calcite shells may be either magnesium or not, and the general principle appears to be that magnesium carbonate associates itself only with calcite with which it is isomorphous and not with aragonite which is of different crystalline form," p. 219.

"The sponges usually do not occur in quantities sufficiently large to form sponge limestones, but the Archaeocyathenae reefs in the Lower Cambrian of the Strait of Belle Isle, Australia, and other parts of the world constitute important limestone formations. In the White Jura of Swabia are massive structureless limestones and dolomites which have been shown to have been built mostly by calcareous sponges. Because of their massive and resistant character the reefs persist after the surrounding rock has eroded away, so that in the Swabian Alps they form isolated crags and outliers, whose easy defense made them the sites of medieval strongholds. Elsewhere in the geologic column and in modern seas the contribution of the sponges are incidental to those of other organisms," p. 224.

"In photosynthesis the calcium carbonate is precipitated as an incrustation more or less over the surface of the plant and in some plants also within the cells and cell walls. The precipitation results from the extraction of carbon dioxide from the water by the plant and consequent reduction of the bicarbonate of calcium to the carbonate, followed by the precipitation of the latter. As the carbon dioxide is taken from the water immediately adjacent to the parts of the plant doing the extracting, it naturally follows that most of the precipitated material is deposited on the plant surfaces, particularly those surfaces having considerable expanse. This work is done by every green plant living beneath a water cover.

"It is probable that the algae do this work to the greatest extent, particularly those belonging to the Chlorophyceae or green algae and the Rhodophyceae or red algae, the former including the Halimeda and Udolea and the latter Corallina, Jania, Melobesia, Lithothamnium, and Lithophyllum. They range from the Tropics to the Arctic regions and usually are abundant in all waters with favorable environments. In Lithothamnium the precipitate forms crusts over the surfaces on which the plant grows; the precipitate in Halimeda is a sieve-like cover about the tips of the algal filaments, and in Acertularia a tube is formed about the stalk of the plant. In Chara and the corallines the lime is deposited in the cells and cell walls of certain parts of the plants. The lime appears to form at first as tiny separate crystals, which ultimately develop into star-like clusters, and these by enlargement unite to form solid structures or layers," p. 232.

The reviewer has believed for some years that the failure to synthesize dolomite in the laboratory under reasonable conditions was due to people working with too pure materials and he has felt that crystallization should be undertaken in presence of ferrous carbonate. It

was therefore a great pleasure to find this theoretical prediction made more plausible, p. 264. "That the sedimentary dolomites were generally and perhaps universally formed under reducing conditions in the presence of dissolved compounds of ferrous iron is shown by the consistent presence of ferrous carbonate in a large number of dolomites which have been tested qualitatively."

"The development of laterites seems to be confined to tropical and sub-tropical conditions, and for their origin various explanations have been offered. Holland suggested that their production might be related to the activties of some lowly organism which required the silica for its activities and hence separated it from the silicates with which it was combined. Maclaren considered that the production of laterite requires tropical heat and vegetation and altering periods of dry and rainy weather. During the dry weather moisture brought to the surface by capillary action evaporates and deposits any matter in solution in and on the surface materials of which some may be replaced. Mead suggested that the reduction of silicates to aluminum hydroxides requires the maintenance of an open texture in clays, and that this depends on the absence of frost. The presence of alkaline waters to leach out the silica would be a favorable factor. According to Maclaren, 'laterites form only on level or approximately level surfaces,' a view supported by Davis. The thickness may attain to 50 or more feet.

"The most significant occurrence of laterite iron oxide in the western hemisphere is in Cuba. The deposits are on plateau-like areas which extend over many thousands of acres, and they range up to about 50 feet in thickness. Considerable alumina not combined with silica occurs with the oxide of iron. There seems to be general agreement that the deposits resulted from the laterization of serpentine, although it has been suggested that the deposits of the Camaguey district are mainly derived from limestone. The large deposits are in the places of formation. There are many local occurrences of which the constituents have been transported from the original place of origin," p. 326.

"Observations made by Kindle on muds artificially dried showed that the sodium chloride was precipitated on the surface in three different forms. An upper layer was pure white and consisted of minute crystals of frost-like appearance. The layer next below was formed of acicular crystals in vertical position and holding a small quantity of clayey matter in the lower part. The third deposit was in the mud cracks and disseminated through the dry mud and consisted of cubical crystals with hopper-like faces," p. 352.

"Grabau has suggested that the Salina salt deposits of New York and adjacent regions developed in a body of water akin to a desert lake. He conceived the salt to have been washed from the Niagara limestones, and due to its greater insolubility the gypsum is supposed to have remained behind. The waters carried the salt to the deeper portions of the Salina basin, where the evaporation of the water deposited the salt as in modern desert basins. The products of disintegration from the surrounding ridges of Niagara limestone are also supposed to have been washed or blown into these basins and to have formed the beds of fine grained limestone interstratified with the beds of salt. In this way it is conceived that the salt would be deposited without the gypsum. As the deposits are without marine fossils, it is assumed that there could have been no connection with the sea. The gypsum which is present is said to lie above the salt, and according to Dana it resulted from the alteration of limestone," p. 363.

"Granular sediments with little or no cohesion between the composing particles are essential to ripple mark formation in water. Ripple mark develops on all types of sands, but is more universal on siliceous sands because of their greater abundance. Mud, marl and other cohesive sediments are never ripple marked by water; when dry and in the form of dust they may be ripple marked by wind. It sometimes happens that a deposit of mud passes abruptly into one of sand; in such a case ripple mark on the sand stops abruptly at the line of contact with the mud. The limitation of ripple mark to granular sediments affords an important clue to the orignal texture of the materials of ripple marked limestones," p. 451.

"During long dry weather the deposits of deltas, flood plains, etc., may crack to depths of many feet. Each time of cracking may lead to a crack forming in a different place, but

the tendency appears to be to follow established lines. Every time of deposition fills all cracks which may be present and the wetting causes wilting about the margins of the cracks. This destroys the bedding and after deposits have passed through this experience for several years they may have undergone a thorough kneading and mixing leading to a considerable loss of stratification and the development of brecciation," p. 496.

"Clay galls develop from the cracking and curling up of thin layers of mud of great cohesion. The hollow cylinders may be rolled for considerable distances by wind and become incorporated in eolian or aqueous sediments. The cylinder then flattens and a thin lenticle of mud results. It is thought that the thin lenticles of green clay common in the Dresbach sandstone of western Wisconsin probably developed in this way," p. 497.

"In tropical and subtropical situations where there is effective downward drainage of ground water through the soil or deposits, oxidation of iron compounds is particularly active, and the resulting colors are generally reddish or brown. Such conditions are characteristic of hillsides, which in turn are not fitted to be places of stable deposition of sediments. Hence, stable red sediments seldom accumulate in the tropical rain belt or other warm and steadily moist climates.

"On the other hand, where a wet season alternates with a hot dry season each year, or where the red lateritic silts are carried from the rain belt out into a drier region with lowered water table, not only are red, brown and purplish soils developed on the hills and other surfaces which are being eroded; but the resulting sediments preserve their reddish colors after deposition, because the effect of the hot dry season with lowered water table even on plains is to burn out the organic matter and leave oxidation full sway. Good illustrations of this principle may be found in the Hawaiian Islands and other abrupt coasts which are exposed to the trade winds. On the continuously wet slopes of such islands the hillside soils are brown or purplish red, but on the river floor plains they are gray and black. On the leeward side of the islands, where there is a short wet and a long dry season, the soils are brick red, and the alluvial deposits have the same color," p. 547.

"Although generally without rainfall, deserts occasionally have water falling in torrents and flowing to the low parts more or less in the form of sheets. The debris of the higher lands is thus washed into the depressions where it is deposited with structures ranging from extreme irregularity to the finest of laminated lake clays. The seasonal rains and glaciers of bordering highlands may bring some water into a dsesert. The volumes of water falling during some of the torrential rains may change the lower parts of a desert region into a vast shallow lake, Russell stating that the Black Rock desert of Nevada has been changed in a few hours from dry burning sands to a lake of 400 to 500 square miles area which in its greatest depths was not more than a few inches deep. This lake was impassable because of the softness of the mud at its bottom, but in a few weeks this became so dry and hard that a horse's hoof hardly made an impression, and was broken into polygons by the mud cracks. Lake Goongarrie of western Australia present a similar change of appearance. This lake is one of the so-called 'dry lakes' and usually it is a 'vast, smooth, bare surface, frequently white owing to a film of salt' but during times of moderate rainfall it becomes a wide sheet of water," p. 554.

Wilder D. Bancroft

Electro-Organic Chemistry. *By C. J. Brockman. 23 × 15 cm; pp. xi + 381. New York and London: John Wiley and Sons; Chapman and Hall, 1926. Price: $5.00.* The book is divided into two parts, reactions at the anode and reactions at the cathode. The anode reactions deal with oxidation of ionized and of non-ionized substances, and also with substitution. The cathode reactions include the reduction of aromatic nitro compounds, the reduction of nitroso compounds, the addition of hydrogen to unsaturated compounds, the reduction of the carbonyl group, and the reduction of compounds containing arsenic, chlorine, sulphur, mercury, etc.

"The speed with which the depolarizer absorbs oxygen is also of importance. There may be added to the electrolyte certain salts which speed up the absorption of oxygen, so that the rate of oxidation as well as the electrical efficiency of the process is increased. For

example, when a suspension of anthracene in 30 per cent sulphuric acid is electrolytically oxidized, the highest yields of 90 per cent are obtained only when a catalyst is added (2 per cent of a cerium salt), the product being anthraquinone. Cerium sulphate is much more active than chromic acid, and may be employed in a cell without a diaphragm. With chromic acid, on the other hand, a diaphragm must be used to prevent the cathodic reduction of the chromic acid. Since the electrolytic regeneration of the chromic acid does not usually keep pace with its reduction to chromium sulphate by means of anthracene, the electrolyte containing the catalyst must be submitted to electrolytic oxidation from time to time. At the anode the cerium salt is oxidized to the ceric condition which carries the positive charge to the organic depolarizer, the result of which is the reduction of the ceric salt together with the oxidation of the organic compound; the former is then immediately reoxidized at the anode to the ceric salt. This transfer of charges bewteen the carrier and the depolarizer does not necessarily take place at the anode, because of the diffusion of the carrier from the anode. Besides certain salts, it has been found that manganese, chromium, and vanadium salts are excellent catalysts," p. 14.

"In only a few instances has the electrochemical oxidation yielded different results from those obtained by the use of ordinary chemical methods. The products are, as a rule, the same as those obtained when hydrogen peroxide is used, so that electrochemical oxidation and oxidation by means of peroxides seem to be somewhat similar mechanisms," p. 18.

"Fichter and Stocker have come to the conclusion that anodic oxygen attacks the nuclear hydrogen before the side chain. This is entirely comparable to the fact that electrochemical halogenation attacks the nucleus only; and Bruner and Dluska have shown that atomic halogen attacks the nucleus while molecular halogen attacks the side chain. This leads to the conclusion that the hydroxylation of the nucleus of cyclic compounds is accomplished at an anode by the action of atomic oxygen, or by the use of silver, or hydrogen peroxides. The application of other chemical oxidation media, such as chromic acid, nitric acid, permanganic acid, etc., leads to products which are not formed by atomic oxygen and therefore must be due to oxidation by molecular oxygen," p. 18.

When discussing the action of inorganic salts in causing the conversion of acetates into methyl alcohol, the author says, p. 29, that "Foerster explains the action of these inorganic salts as due to the fact that the congestion of their anions at the anode decreases the concentration of the organic anions there, thus diminishing the number of the organic anions discharging at the anode while the number of OH' ions discharging remains nearly constant. Then these anions unite to form an ester which is immediately hydrolyzed in the aqueous solution to the alcohol and the inorganic acid. This has been criticized by Moser on the ground that the formation of these esters with inorganic acids by electrolysis cannot be detected, and therefore it is not certain that the esters so formed would under the prevailing conditions be so easily hydrolyzed as Foerster's theory supposes," p. 29.

"The material from which the anode is made seems to influence the course of the reaction to as great an extent as does a change in temperature and current density. Anodes of smooth platinum and iridium yield mostly ethane while iron and palladium under identically the same conditions yield mostly oxygen and not a trace of ethane. Midway between two extremes, platinized platinum electrodes yield a mixture of oxygen and larger amounts of oxidation products. . . . The different behavior of these electrodes is connected with the varying potential at which oxygen is liberated at them; the potential required for the formation of ethane lies below that at which oxygen is evolved at platinum or iridium anodes but above the value for iron and palladium anodes," p. 37.

"A concentrated solution of potassium butyrate yields at the anode a mixture of gases which, after the carbon dioxide has been removed, consists of propylene and only a trace of oxygen and hexane," p. 39. "The electrolysis of the potassium salt of normal butyric acid in the presence of inorganic salts yields isopropyl alcohol with a considerable amount of the normal alcohol. When perchloric acid is added, the formation of hexane predominates, though propyl alcohol and propionic aldehyde are also formed," p. 40.

"A most interesting oxidation of lactic acid to pyruvic acid has been accomplished by electrolytic means. Pyruvic acid, being rather rich in oxygen, is necessarily more or less

unstable in the presence of electrolytic oxygen, is further oxidized to various degradation products. However, by an ingenious use of electrolytes and experimental conditions Smull and Subkow were able to stop the electrolytic oxidation of pyruvic acid. Under normal conditions no pyruvic acid could be detected in their products of electrolysis. But when copper lactate in the presence of copper nitrate, so that the copper concentration of the system was not lower than 20 per cent, was electroyzed with a current density of 0.04 ampere on a platinum foil anode, the pyruvic acid formed momentarily was removed from the solution by the copper ions as the insoluble precipitate of copper pyruvate. Lead acted about as well as copper in removing the pyruvic acid from the sphere of oxidation. Alkaline, neutral and acid solutions yielded no pyruvic acid. This is an excellent example of what can happen if an unstable or a transient compound can be removed from the sphere of depolarization as a means of protecting it from further action," p. 49.

One does not quite see why the conversion of acetylene into acetaldehyde should be called an oxidation, p. 79. "Glycols may be made from ethylene or gases containing ethylene, using a solution of sodium chloride which is sufficiently conductive for industrial uses with or without a diaphragm and electrolyzing between electrodes which may be of platinum, carbon, or lead with an oxide catalyst of chromium, manganese, or cerium," p. 80.

"In an alkaline solution ammonia is oxidized at a Pt electrode to nitrogen, nitrous oxide and nitrate, but at anodes of Cu, Ni, Co, and Fe, besides nitrogen, some nitrate is formed especially at the copper anode. When copper oxide is present, the oxidation goes completely to nitrate without the formation of gaseous compounds. It will not be necessary to go any further into the formation of inorganic nitrogen compounds at this point. We are interested only in the organic derivatives," p. 97.

"It is well known that formamide can be oxidized in an ammoniacal solution to carbamide by purely chemical means, which fact gave Fichter the key to the starting point. The series of compounds primarily formed in the oxidation of ammonia may be indicated as the reverse of the reduction of nitro compounds, *i. e.*,

$$HNH_2 \longrightarrow HNHOH \longrightarrow HNO \longrightarrow NO_2' \longrightarrow NO_3'$$

in which scheme HNO has not been isolated.

"Evidence points to the fact that only those organic compounds which first form formamide as an intermediate product may be electrochemically oxidized in an ammoniacal solution. The reaction then will be:

$$2NH_2COOH + 2NH_2OH \longrightarrow HCONH_2 + H_2N_2O_2 + H_2O$$

and the $HCONH_2$ is further oxidized to carbamide in the presence of an excess of ammonia. Fichter explains the failure to detect hydroxylamine and hyponitrous acid in the reaction mixture as being due to their immediate reduction. Müller and Spitzer found that the gaseous and dissolved products of the oxidation were less by 20-30 per cent than that calculated from the current used, which would be accounted for by the escape of nitrous oxide. Explosion experimeents also seem to indicate the presence of nitrous oxide among the gaseous products of the oxidation of an ammonium carbamate solution," p. 97.

"The purely chemical oxidation of dimethylaniline by lead dioxide in sulphuric acid does not result in good yields, but the electrochemical oxidation at a lead dioxide anode yields good amounts of tetramethylbenzidine, tetramethyl-diaminodiphenylmethane with traces of trimethyl-phenyl-*p*-phenylenediamine; at a platinum anode the first and third compounds are the main products and the second appears in traces," p. 116.

"The electronic conception of valence developed by Fry assumes that in the chlorination of benzene and its homologues, a carrier acts as a source of positive halogen, and, in the case of water being present, the chlorine first reacts with the water:

$$Cl_2 + H_2O \leftrightarrows HCl + HOCl$$

The hypochlorous acid formed then acts as a source of positive chlorine which replaces positive hydrogen in the benzene. An attempt has been made to verify this mechanism. With chlorine and benzene in the presence of water, substitution was obtained. Under identical conditions, with anhydrous materials, no substitution took place, but a considerable amount of benzene hexachloride was produced. As the results with water were duplicated when

light was excluded from the system, there was, obviously, no photochemical action, and the effect was due entirely to water, which probably acts as suggested by Fry," p. 162.

"Carbonic acid may be reduced under a variety of conditions. A pure aqueous solution of carbonic acid yields traces of formic acid. A strongly acid solution also yields traces of formic acid though this is not the case in a neutral solution. There is no reduction at iron, platinum, copper, or nickel cathodes; there is, however, a good reduction when the electrodes are of mercury, amalgamated zinc, or amalgamated copper. It seems that the reduction takes place only when the hydrogen is produced at an electrode with a large overvoltage. The fact that a bicarbonate solution yields the best results is an indication that it is not the undissociated acid that is reduced nor is it the carbonate ion, CO_3'', but rather the bicarbonate ion, HCO_3', which acts as the depolarizer at the cathode. Lead cathodes have been shown to work well under certain conditions. Electrolytic zinc, amalgamated copper and specially prepared lead cathodes also give good results.

"If the carbon dioxide is led through the solution at high pressures, the reaction goes much more completely. At fifty atmospheres pressure the current yield of formic acid is forty-nine percent," p. 308.

The author is not strong on explanations. Some people would like to know in regard to the oxyhydrogen coulometer, p. 4, why the freshly filled cell should be used alone for a time, because fresh alkali has a tendency to foam." Why should electrolysis of a fused mixture of lead and sodium acetates give considerable amounts of ethane, p. 44, when lead and zinc acetates give chiefly methane? It is not at all clear why electrolytic chlorine should react with benzene more slowly than does free chlorine, p. 160. The reviewer cannot endorse the statement, p. 23, that "when the alkali salts are electrolyzed, the alkali ion is discharged at the cathode."

The book is invaluable as a compilation. *Wilder D. Bancroft*

Exercises in General Chemistry and Qualitative Analysis. *By H. G. Deming and S. B. Arenson. Second revised edition. 22 × 15 cm; pp. xii + 284. New York: John Wiley and Sons, 1926. Price: $1.80.* In the preface to the first edition the authors say that an elementary course in chemistry has, in fact, three chief aims: 1. To make the student familiar with a few representative types of matter; 2. To reveal some of the general principles that govern the transformations of matter; 3. To afford some experience with the experimental methods by which chemistry has won its advances.

In the preface to the second edition the authors say: "Though a number of quantitative exercises have been retained, the authors are of the opinion that quantitative work in an elementary course often consumes time that were better spent in the accumulation of useful and necessary qualitative information."

The experiments are grouped under the headings: introductory; states of matter; weight relations in chemical change; oxygen; hydrogen; water and solutions; acids, bases, and salts; valence; chemical reactions; chemical arithmetic; molecular weights and chemical formulas; chlorine; the halogens; reaction velocity; hydrogen sulfide; sulfuric acid; the ionic theory; nitrogen and ammonia; nitric acid; phosphorus; organic chemistry; colloids; general properties of the metals; electrochemistry; miscellaneous; qualitative analysis.

There are a number of admirable experiments, such as the preparation of hydrogen from iron and steam, p. 59; the precipitation of sulphides, p. 130; the preparation of sulphuric acid, p. 137; the relation between ionization and conductance, p. 140; etc. The reviewer believes in making the introductory chemistry tie in with qualitative analysis, which was not done when he was an undergraduate.

There are some slips. The law of Graham, p. 22, does not hold for free diffusion. On p. 27 the authors say that a constant freezing-point indicates that a substance is pure. They add that engineers are interested in the freezing-points of alloys, as a means of determining their identity and purity. By definition an alloy is not a pure substance except when it consists of a compound and by the authors' definition a eutectic mixture is a pure substance. The reviewer wonders how accurately one determines copper by precipitation with aluminum, p. 42, and whether it is desirable to introduce a silica jelly quite so casually as is done in the experiment on the lead tree, p. 45. *Wilder D. Bancroft*

1 - 15

FIFTH REPORT OF THE COMMITTEE ON CONTACT CATALYSIS*

BY E. EMMET REID

Introduction

There is among chemists a growing tendency to forget the distinction between catalyzed and non-catalyzed reactions. Catalyzed reactions used to be considered exceptional and therefore remarkable. As we find more and more of such reactions their exceptional nature disappears. Soon all reactions will be catalytic and then this term will cease to be descriptive. We are coming to face two more fundamental questions: 1) Why do chemicals react at all? and 2) Why do they not always react instantly when brought in contact with each other, provided the energy change would be in the right direction? We shall probably not get a clear answer to either of these until we come to a much more complete understanding of atomic structure. The union of one atom with another is due to the transfer of one or more electrons or to the mutual holding of one or more pairs of electrons. Hence the study of reactions is reduced to finding out why and how the electrons readjust their relations with atomic nuclei. We are far enough along to see that this must be so but the investigation of atomic structure has not progressed far enough to answer the many questions that arise.

The distinction between homogeneous and heterogeneous catalysis is gradually vanishing. The radiation theory of catalysis in its original restricted form seems to be fast losing ground. The intermediate compound theory appears to be gaining in acceptance but losing in definiteness. Perhaps it would be better to change "intermediate compound" to "intermediate complex" since the stoichiometric relations implied by "compound" may exist but seldom. Combination and adsorption are probably not as different as we used to think them. X-ray photography has shown us that in a crystal of sodium chloride there are no molecules to be represented by Na-Cl in which a univalent sodium atom is combined with a likewise univalent chlorine atom. We find that each sodium atom is directly joined to eight chlorine atoms and that each chlorine atom is similarly joined to eight sodiums. If the joining of atom to atom is thus indiscriminate within the crystal why should it be limited to strict valence relationships at the surface of a mass? The surface atoms can not be linked with the proper number of atoms and must satisfy their affinities by adsorbing vapors or gases. Whatever we may call the forces that bind the sodium atom to the eight surrounding chlorine atoms, they are nevertheless forces. These forces when not satisfied, as they cannot be at the surface of a crystal, must reach out for something that can be adsorbed. The

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adsorbed layer is held by the same forces that hold the atoms together within the mass. As a matter of fact we find adsorbed films on all surfaces. If the sodium and chloride atoms are joined promiscuously in the solid sodium chlorine, what happens when melting takes place? The relations can not be very different in the molten material, yet there is freedom of motion: the atoms must be able to shift their unions from one to another as they pass. This labile state of the unions may be the explanation of the greatly enhanced reactivity of substances in the liquid state. Adsorptive power becomes solvent power and all manner of substances are dissolved as they come in contact with the liquid. We may picture the solute as being adsorbed on the surface of the liquid in consequence of the unbalanced forces that exist there. On account of the mobility of the liquid the surface layer would not remain as such but would mix with the rest of the liquid leaving a fresh surface to repeat this process. The adsorptive forces may be so strong that the adsorbed molecule is pulled apart in the process. This may be what happens when a molecule of hydrogen chloride is adsorbed by a water surface. If a polar molecule is thus disrupted, the fragments will carry charges and be ions. Solution and adsorption are both highly selective. We know that the reactivity of any substance is greatly enhanced when it is dissolved: it is probably likewise increased by adsorption. If the two processes are essentially the same, there is no reason for distinguishing between homogeneous and heterogeneous catalysis.

The old conception according to which the catalyst contributes only its presence and takes no part in the reaction has been given up. Zelinsky[1] remarks: "My observations on catalysis extending over several years have brought me to the same view of catalytic phenomena as was expressed by Mendelejeff[2] long ago in such a simple and original form, a view which later Raschig[3] and recently it seems Bodenstein[4] have adopted. In the contact processes with carbon compounds, the catalyst does not determine the reaction simply by its presence but by taking the rôle of an active principle in the process; its surface energy produces far-reaching alterations in the substances which come into contact with it."

The Fourth Report of this Committee written by H. S. Taylor was devoted to the exposition of one point of view and did not include a general survey of catalytic literature. A different plan has been followed in the present report and an attempt has been made to cover the field more generally for 1925 as well as 1926. The references were obtained chiefly by searching Chemical Abstracts. In all, 240 articles have been noticed though there is no claim of completeness. Only abstracts of some of these were available. The most of the space has been devoted to articles on the theories of catalysis but large numbers of others have been catalogued with brief statements of results accomplished.

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[1] Brennstoff-Chem., **7**, 207 (1926); Ber., **59**, 15 (1926).
[2] J. Russ. Phys. Chem. Soc., **18**, 8 (1886).
[3] Z. angew. Chem., **19**, 1985 (1906).
[4] Ann., **440**, 177 (1924).

General Articles and Addresses

Two important summaries and discussions have been published, one on homogeneous catalysis by Hinshelwood[1] who, with his coworkers, has made many important contributions to this field and the other on auto-oxidation, anti-oxygenic and pro-oxygenic activity by Moureu and Dufraisse[2] who have made many and remarkable discoveries on the acceleration and retardation of oxidation. These papers cover these fields much more thoroughly than can be done in the present report. Reference must be made to them for a fuller discussion.

An important paper by Armstrong and Hilditch[3] gives a summary of our knowledge of catalysis at that date. The views are very similar to those expounded by Taylor in the Fourth Report. The same authors[4] have reviewed hydrogenation. Bone and Andrew[5] give an excellent statement of results so far achieved in explaining surface catalysis.

In an address, Taylor[6] gives a fine view of the field of catalysis. The most useful catalysts for each type of reaction are tabulated. Many important facts as to reactions at boundaries are brought together. In another address the same author[7] sketches the industrial developments due to catalytic investigation.

Two masters of the art describe their own work: Sabatier[8] tells in an intimate retrospect of his great achievements how he was led to his hydrogenation method and Patart[9] gives a detailed description of his methanol process. The industrial production of synthetic methanol is discussed by Lormand[10]. Mittasch,[11] who has spent a score of years in the catalysis research laboratory of the Badische Co. gives, in an address before the German Chemical Society, a fine account of the history and achievements of catalysis.

Rideal[12] reviews catalysis from the point of view of Rayleigh, Hardy and Langmuir, who have established that the seat of catalytic activity is limited to the film of reacting substances adsorbed on the surface of the catalyst.

Tweedy[13] gives an excellent statement of the theories of catalysis. Guiselin[14] covers the same subject with particular emphasis on the importance of porosity

[1] Chem. Rev., **3**, 227-256 (1926).
[2] Chem. Rev., **3**, 113-162 (1926).
[3] Chemistry and Industry, **44**, 701 (1925).
[4] Deuxième Cons. Solvay, 1926, 492.
[5] Proc. Roy. Soc., **109A**, 459 (1925).
[6] Canadian Chem. Met., **10**, 35 (1926).
[7] Ind. Eng. Chem., **18**, 958 (1926).
[8] Ind. Eng. Chem., **18**, 1005 1926).
[9] Bull. soc. enc. ind. nat., **137**, 1417; Chem. Abs., **19**, 2026 (1925); Chimie et industrie, 13, 179 (1925).
[10] Ind. Eng. Chem., **17**, 430 (1925).
[11] Ber., **59**, 13B (1926).
[12] Deuxième Cons. Solvay, 454 (1926).
[13] Chemistry and Industry, **45**, 157-9, 177-80 (1926).
[14] Mem. Compt. rend. soc. ing. civ. France. **78**, 25 (1925).

and surface action. He suggests making catalysts with pores of known size and shape. Swientoslawski[1] classifies catalytic reactions in two groups:

1. Those that are allowed to reach a stable equilibrium.

2. Those in which the reactants are removed from the influence of the catalyst before a stable state is reached.

Seymour[2] and Pascal[3] discuss catalysis in industry. Firth[4] writes of catalysts and enzymes. Almquist[5] describes catalysis at high pressures.

We have sets of lecture demonstrations by Webster[6] and by Kolthoff.[7]

Critical Increment

There is a general agreement that the reason that reactions in homogeneous mixtures do not take place instantaneously and completely is that at any one time only a few of the molecules have the necessary amount of energy. Those that have this are said to be in the "excited" state and the amount of energy required to put a molecule in this state is called the "critical" increment." The theories of catalysis differ from each other in the mechanism which is proposed by which this critical increment can be imparted to a molecule.

In a thorough mathematical paper G. N. Lewis and Smith[8] consider the possible sources of the energy required for activation. They conclude "that there is no valid argument against the general radiation hypothesis. On the other hand, the special radiation hypothesis, as announced in the first papers by Perrin and W. C. McC. Lewis, in which it is assumed that ordinary chemical reaction is caused by nearly monochromatic radiation, is not tenable. Not only is there no experimental evidence in its favor, but it is certain that the number of collisions between the molecules and such very restricted light quanta would be inadequate to account for the observed rates of reaction. It is shown that both collisions and radiant energy offer opportunities for the activation of molecules far greater than the number required to account for observed reaction rates."

In a similarly thorough paper Tolman[9] discusses "the various mechanisms of chemical activation that have been proposed, in order to estimate their possible importance for chemical reaction." He concludes that "activation by collision with molecules of high enough kinetic energy cannot take place fast enough to account for the decomposition of nitrogen pentoxide or other unimolecular gas reaction. Activation by collision also could not take place fast enough to account for the decomposition of nitrous oxide or other bimolecular reactions, if the total energy of activation is brought into the reaction by one of the two molecules. . . . Activation, in accordance with the

[1] J. Chim. phys., **22**, 73 (1925).
[2] Industrial Chemist, **2**, 226 (1926).
[3] Technique moderne, **17**, 757 (1925).
[4] Chem. Age (London) **14**, 324, 348 (1926).
[5] J. Chem. Ed., **3**, 385 (1926).
[6] Chem. Weekblad, **22**, 317 (1925).
[7] Chem. Weekblad, **22**, 356 (1925).
[8] J. Am. Chem. Soc., **47**, 1508 (1925).
[9] J. Am. Chem. Soc., **47**, 1524 (1925).

simple radiation theory, by the adsorption of the frequency calculated by assuming the energy of activation to be taken up as a single quantum, cannot take place fast enough to account for the decomposition of nitrogen pentoxide, or other unimolecular reactions, and leads to incorrect predictions as to the frequencies that will be active. . . In conclusion it can be stated that activation may occur to some extent by all the four mechanisms suggested. Indeed, since the great difficulty is to account for the rapidity with which the energy of activation is supplied, we must not despise the assistance afforded by any method of activation. However, it seems at the present as if our main hopes must be centered on the elaborated radiation theory."

Cofman-Nicoresti[1] regards the catalyst as "a separator of heat from other elements in a reaction." Wolfenden[2] in a study of the critical potentials of hydrogen in presence of catalytic nickel and copper, concludes that substantial quantities of atomic hydrogen are present on these metals. The ionization curve in presence of the catalytic metal resembles that of an incandescent grid.

Theory of Surface Action

In the Fourth Report of this Committee, H. S. Taylor[3] has developed in fine fashion the theory of catalytic action on a surface. His ideas have gained general acceptance and have had a great influence on recent investigations. The remarkable magnitude of the heat of absorption of oxygen on charcoal observed by Garner[4] led him to believe "that the valency of the surface carbon atoms is very far from being satisfied by the neighboring carbon atoms." He feels that the difference beween the reactions of carbon and oxygen and a catalytic reaction lies in the fact that the atoms of the catalyst do not leave the surface although their relative positions with respect to one another may change during the reaction. It is, however, clear that those atoms lying in an exposed position on the surface, by virtue of their high energy content, will play a large part in the chemical process. They will be the most likely to possess the energy necessary for promoting the trigger action of catalysis. Also, it can be seen why the surface becomes increasingly effective with use. If part of the heat liberated during the heterogeneous reaction is absorbed by the surface, this may result not only in an increase in the total surface but also in an increase in the proportion of exposed atoms on the surface, *i.e.*, an increased free energy of surface per sq. cm. "It is not unlikely that a comparatively small number of the total atoms on the surface are the active agents in promoting chemical change."

The action of a catalytic surface has been studied by Hinshelwood and his coworkers in a series of papers. Hinshelwood and Pritchard[5] explain the decomposition of nitrous oxide on a hot platinum wire by assuming that "the nitrous oxide gives its oxygen atom to the bare platinum surface . . . the

[1] Pharm. J., **115**, 345 (1925).
[2] Proc. Roy. Soc., **110A**, 464 (1926).
[3] J. Phys. Chem., **30**, 145 (1926). See also Proc. Roy. Soc., **108A**, 105 (1925).
[4] Nature, **114**, 932 (1924).
[5] J. Chem. Soc., **127**, 327 (1925).

function of the surface is thus to act as an acceptor for atomic oxygen, thereby rendering possible an unimolecular in place of a bimolecular process. What makes the odd oxygen atom more easily detachable is its affinity either for the platinum or for atomic oxygen already on the platinum." Green and Hinshelwood[1] have studied the decomposition of nitric oxide on platinum and believe that this "provides a further example of a reaction that is bimolecular in the gas phase becoming unimolecular at the surface of a catalyst. The reaction NO = N + O is therefore rendered possible without the communication of energy in prohibitive amounts."

Hinshelwood and Pritchard[2] have investigated the reaction between hydrogen and carbon monoxide on a platinum wire at 1000°. They say: "We must therefore assume that the catalytic activity of the surface is localized in certain active points forming a small fraction only of the total surface. A simple mechanism which now accounts for most of the facts is that reaction occurs when hydrogen and carbon dioxide become adsorbed adjacent to each other on an active part of the surface. It must be assumed further that the fraction of the active surface covered by carbon dioxide increases from zero to nearly unity as the pressure of carbon dioxide increases from 0 to 400 mm, while the adsorption of hydrogen on those points left free from carbon dioxide is never very great, so that we have to deal with that portion of the hydrogen adsorption isotherm where adsorption is more or less directly proportional to pressure."

In the second paper they find: "The adsorption of each gas on the active centers of the catalyst is almost independent of the pressure of the other gas. This shows that not all the surface is active, but that only certain parts are able to adsorb hydrogen and carbon dioxide and cause them to react. The parts which adsorb hydrogen in this way are different from those which adsorb and render active the carbon dioxide. Interaction apparently takes place when molecules of the two gases are adsorbed on adjacent centers of the appropriate kind."

The same authors[3] find that the decomposition of hydriodic acid on a gold surface is of the zero order and is uninfluenced by the pressure of the hydrogen. "The function of the surface in the catalyzed decomposition reactions of nitrous oxide on platinum, hydriodic acid on gold and ammonia on tungsten is to permit the occurrence of a unimolecular instead of a bimolecular process requiring an energy of activation about twice as great."

Hinshelwood and Burk[4] have studied the decomposition of ammonia and of hydriodic acid on various surfaces and confirm the above views. "Hence we must conclude once more that different reactions are provoked at different points ("active centers") on the catalytic surface."

Hutchinson and Hinshelwood[5] have studied the interaction of hydrogen and nitrous oxide on the surface of a gold wire. "The results can be inter-

[1] J. Chem. Soc., **1926**, 1709.
[2] J. Chem. Soc., **127**, 806, 1546 (1925).
[3] J. Chem. Soc., **127**, 1552 (1925).
[4] J. Chem. Soc., **127**, 1105, 2896 (1925).
[5] J. Chem. Soc., **1926**, 1556.

preted by assuming that hydrogen and nitrous oxide are adsorbed on the surface independently of each other, and that interaction can take place between adjacent molecules. . . . A second effect was traced to hydrogen, namely a steady decrease in the activity of the wire, especially when it was heated in mixtures containing hydrogen in excess. . . . It is suggested that hydrogen gradually disssolves in the body of the metal—this solution being distinct from its primary adsorption on the surface—and decreases the adsorptive power towards nitrous oxide."

Burk[1] goes further into the details of adsorption by assuming that the two ends of a molecule are independently adsorbed by active points on the catalytic surface. If these points are further apart than the normal length of the molecule, it would be stretched and the energy required to break it up thereby lessened.

Faresti[2] also believes that the surface of the subdivided nickel is constituted of adsorbing centers of various power and that the catalytic activity depends on which centers are capable of adsorbing the gas from the strongest bonds.

The activity of a copper catalyst is found by Palmer and Constable[3] to vary periodically with the temperature of reduction from the oxide, there being three maxima between 220° and 420°. They[4] observe that "the rates of dehydrogenation of the primary alcohols, ethyl, propyl, butyl, isobutyl and isoamyl are all equal within the limits of experimental error; and the temperature coefficient of the velocity is the same for all. . . . Secondary propyl alcohol reacts with a velocity about five times that of the primary alcohols.

"Reaction occurs in an adsorption film covering the copper surface. The film becomes one molecule thick at 280°C. and its thickness increases as the temperature falls. All primary alcohols contain the $-CH_2OH$ group at the end of the hydrocarbon chain. The rate of dehydrogenation has been shown to remain constant while the length of the hydrocarbon chain is doubled. It is very improbable, considering the very specific action of catalysts, that reaction could be initiated at a distance from the surface. These observations, therefore, show that the primary alcohols are adsorbed, the $-CH_2OH$ group in contact with the surface, and the hydrocarbon chains in contact perpendicular to the copper surface."

Constable[5] maintains that "chemical reactions occur only when alcohol molecules are adsorbed over a characteristic arrangement of copper atoms." In a second paper he[6] finds that "if the molecules only react in the unimolecular film next to the catalyst surface, then varying the pressure only affects the change in so far as it affects the life of a molecule in the surface layer. . . . Hence the reaction velocity should be practically independent

[1] J. Phys. Chem., **30**, 1132 (1926).
[2] Gazz., **55**, 185 (1925),
[3] Proc. Roy. Soc., **106A**, 250 (1924).
[4] Proc. Roy. Soc., **107A**, 255 (1925).
[5] Proc. Roy. Soc., **107A**, 270 (1925).
[6] Proc. Roy. Soc., **107A**, 279 (1925).

of the pressure, provided the catalyst is completely covered with the adsorbed alcohol film." In two further papers Constable[1] considers the effects of diluents on the rates of surface catalysis. Assuming the theory of catalytic centers he arrives by mathematical analysis at a formula which he verifies for the dehydration of alcohol over copper. The same author[2] gives a mathematical treatment of the dynamics of surface action in a closed vessel. The formulae arrived at are verified by experiments. While the activity of a metallic surface depends on the method of preparation, Levi[3] finds no difference in the performances of thoria catalysts made in seven widely different ways.

Gauger[4] found thin films of platinum or nickel on Pyrex glass to be inactive and concludes that the importance of mere extent of surface has been overestimated. "It seems not at all unlikely that a catalyst may have electrons that are on somewhat different energy levels than in the case of the crystalline metal. The so-called active surface of the catalyst consists, therefore, of those molecules that have electrons in these outer energy levels."

Almquist and Crittenden[5] find that copper reduced from the oxide is much more effective than massive copper in removing oxygen from mixtures of hydrogen and nitrogen.

Hoover and Rideal[6] have studied the decomposition of ethanol over thoria. They find both dehydration and dehydrogenation. They conclude that "the theory that the two reactions are promoted by different active areas or patches on the surface has been shown to offer a satisfactory explanation of the observed phenomena. Support for this theory is found from the fact that the two reactions require different energies of activation, that poisons cut down one reaction to a greater extent than the other, that chloroform promotes the ethylene reaction, and that the ratio of the reaction velocities of the two reactions is altered at low pressures. . . . It seems likely that both the orientation of the surface atoms and the adsorptive power of the active patch play a part in determining the type of reaction that proceeds on the active patch. At atmospheric pressure the reaction velocities depend in part on the poisoning effect of the products of reaction."

Constable[7] prepared copper in many different ways and measured its activity. A smooth copper surface is probably less than 1/5000 as active as the same area of reduced copper. "The essential feature necessary to the production of copper catalytically active in the dehydrogenation of alcohols is the sudden liberation of free copper atoms under conditions in which the kinetic energy of the atoms of the structure is insufficient to cause the collapse of the active centres. Thus methods of producing copper under the same

[1] Nature, **116**, 278 (1925); Proc. Camb. Phil. Soc., **23**, 172 (1926).
[2] Nature, **117**, 230 (1926).
[3] Atti. Accad. Lincei, (6) **2**, 419 (1925).
[4] J. Am. Chem. Soc., **47**, 2278 (1925).
[5] Ind. Eng. Chem., **18**, 866 (1926).
[6] J. Am. Chem. Soc., **49**, 104 (1927).
[7] Proc. Roy. Soc., **110A**, 283 (1926).

physical conditions should give copper with the same surface activity and showing the same temperature coefficient. In spite of the wide divergence between the spacing of the copper atoms in copper formate and valerate thermal decomposition gives a product showing very nearly the same temperature coefficient and surface activity.

"Since the surface fields vary with the nature as well as the arrangement of the surface atoms, the nature and the magnitude of the molecular distortion will vary with the chemical nature and physical state of the surface, and we have an explanation of the specific action of catalysts. It is apparent that very small quantities of added material of suitable physical properties could cause wide variation in the nature and distribution of the centres of activity, and we have a tentative explanation of promoter action.

"The persistence of the centres of activity unchanged by chemical reaction requires that the adsorption and desorption of the reactants shall be reversible without alteration of the surface; and that the heat absorption or evolution shall not sinter the existing centres of activity during reaction. Many chemical changes are violent enough to cause marked changes in the surface. In these cases the activity of the surface increases on use to a maximum, which corresponds with the maximum number of centres capable of existing together at a given instant."

Fryling[1] regards some of the surface atoms of a nickel catalyst as being in an almost gaseous condition which he considers as corresponding to a high temperature. He assumes "that active nickel atoms dissociate hydrogen molecules." Heat treatment of a catalyst reduces the heat of absorption. This reduction is less in the case of a promoted catalyst.

An interesting extension of his former theories is given by Taylor[2] to explain the dual action of oxide catalysts. "It is significant that, in the case of formic acid decomposition, in presence of metal catalysts the reaction products are exclusively those of dehydrogenation: hydrogen and carbon dioxide, irrespective of the metal. With oxide catalysts, on the other hand, the products may be dehydrogenation as, for example, with zinc oxide, or mainly dehydration as, for example, with aluminium oxide. To what can this variation be attributed? A metal surface is composed of metal ions and electrons, an oxide surface of metal ions and oxide ions. The conclusion seems inevitable that, on the metal ion (positively charged) the dehydrogenation process occurs, whilst on the oxide ion, dehydration occurs. Attachment to the positive ion has the effect of giving the hydrogen atoms in the formic acid molecule greater freedom, in agreement with the observation made above that substitution by an electrogenative substituent such as chlorine causes the hydrogen ion to have greater freedom. The negative oxide ion causes the hydrogen atoms to be more firmly attached and so the dehydration split is favored. On this basis, an oxide catalyst surface is to be regarded as composed, not of a single catalyst, but of two catalysts, metal ions and oxide ions and the

[1] J. Phys. Chem., **30**, 818 (1926).
[2] Fourth Colloid Symposium, 19 (1926).

nature of the changes induced in the adsorbed reactant is determined by the charge of the ion on which the reactant molecule is adsorbed. The extent of the two alternative changes will be determined by the relative extent of adsorption of reactant on the two ions, on the relative frequency of the two ions in the surface and on their specific individual catalytic activities. These several factors, extent of adsorption, frequency of ions in the surface and catalytic activity will be determined by the degree of saturation of the lattice ions (*i.e.*, catalyst structure) and by the extent to which the ions are already covered by poisons (salts, ammonia, water, etc.)"

Russel[1] adopts the view that, for chromium, manganese, iron, cobalt and nickel, the number of electrons in the outermost orbit is between one and two and is, therefore, either one or two. The consequence is that these atoms can never be electrically neutral in the sense that other atoms are. Hence each of these metals has an active and a passive state according as the outer orbit contains two electrons or only one. These metals "adsorb gases and act as catalysts when in the passive form. They adsorb because of their property of never being electrically neutral" and they catalyse a reaction "because of their potentiality of passing from the passive to the active form."

Tzentnershver and Steaumanis[2] have measured the over-voltages of various metals and compared them with the catalytic effects of these metals on rate of solution of zinc in acids. The orders of magnitude turned out to be entirely different.

Baudisch and Welo[3] have investigated active ferric oxide made by heating in oxygen to 330° and inactive which had been heated to 550°. The X-ray spectrograms were entirely different. They conclude that the catalytic activity is connected with the "spatial arrangements of the electrons and protons in the atom. . . . The activity seems to depend on the size of the crystals and upon the intramolecular arrangement and not upon the presence of Fe" nor on the adsorptive capacity."

Levi and Haardt[4] in a study of the relation of catalytic activity to extent of surface have determined particle size of a platinum catalyst. The area decreased with heat treatment. The following were the areas of 0.01 g. catalyst at different temperatures: 60°, 5588 sq. cm.; 110°, 5050; 150°, 3300; 180°, 1880; 215°, 1385. "The experiments indicate that the catalytic power of a metal is predominatingly a function of its surface area." On the contrary Rocasolano[5] holds that the effectiveness of catalysts depends on composition rather than on physical properties. He thinks that platinum particles have a shell of oxide which is alternately reduced and oxidised.

According to Rice[6] many of the systems which have been regarded as homogeneous are quite otherwise. As ordinary distilled water contains some

[1] Nature, **117**, 47 (1926).
[2] Z. physik. Chem., **118**, 438 (1925).
[3] Chem. Ztg., **49**, 661; J. Biol. Chem., **65**, 215 (1925).
[4] *Gazz.*, **56**, 424 (1926); *Atti. Accad Lincei*, (6) **3**, 91, 215 (1926).
[5] Nat. Ges. Wiss. Göttingen, 1924, 177.
[6] J. Am. Chem. Soc., **48**, 2099 (1926).

25,000 suspended particles per cc., some reactions, at least, may be confined to the surface of these particles. "The thermal decomposition of hydrogen peroxide is an example of a reaction that is to some extent catalyzed by the walls of the vessel but mainly by suspended dust particles; when hydrogen peroxide, free from dust, is kept in a vessel of fused silica it is a remarkably stable substance and may be heated for several days to 60° without appreciable decomposition." He suspects that in many reactions the real catalyst is the suspended dust which is promoted or poisoned by other substances. Dust may be responsible for anomalous results in many supposedly homogeneous reactions. Many of the theories previously put forward relative to the decomposition of hydrogen peroxide may require revision.

Adsorption and Catalytic Activity

Since it is generally admitted that adsorption by a surface is necessary fo catalytic effect it is natural that many investigations have been made to relate the two quantitatively. While catalysis may not be possible without adsorption, it is certain that adsorption takes place frequently without leading to any chemical change. The conclusion from many measurements is that, while the two are closely related, the one does not follow the other according to any mathematical relation.

Alexeyevskii[1] has measured the adsorption of 72 organic compounds and bromine by animal charcoal and by calcined copper sulphate.

Hoskins and Bray[2] find that manganese dioxide, copper oxide, and mixtures of the two adsorb larger amounts of carbon monoxide than of any other gas. The rate of adsorption of carbon monoxide by one of these is in general closely related to its activity in oxidizing this gas.

Firth and Watson[3] conclude that the catalytic activity of charcoal in the decomposition of hydrogen peroxide is not related to its capacity for absorbing iodine from a chloroform solution.

Lazier and Adkins[4] have measured the adsorption of ethylene and hydrogen by zinc oxide, ferric oxide, nickel, and copper; and also hydrogenation rates with these catalysts. They say that: "The results of the adsorption and catalytic activity measurements indicate that there is a qualitative agreement between the two manifestations of chemical activity, but there is apparently no quantitative relationship between total adsorption and catalytic activity."

Duclaux[5] assumes that atoms or molecules which are brought in contact with one another give addition compounds. . . . These addition compounds are formed spontaneously, *i.e.*, either without activation or, more probably, by autoactivation. Adsorption is but a particular case of the formation of these compounds. . . . These addition compounds can undergo, either without activation or by autoactivation, an internal transposition

[1] J. Russ. Phys. Chem. Soc., **55**, 401 (1924); Chem. Abs., **19**, 2634 (1927).
[2] J. Am. Chem. Soc., **48**, 1454 (1926).
[3] J. Phys. Chem., **29**, 987 (1925).
[4] J. Phys. Chem., **30**, 353 (1926).
[5] "Deuxième Cons. Solvay," 630-45; Chem. Abs., **20**, 3614 (1926).

which can in turn be followed by dissociation. Under these conditions the function of the catalyzer consists essentially in allowing of a *transposition* which is equivalent to a reaction which, in its absence, would take place with difficulty and in low yield, or else at a higher temperature."

Pearce and Alvarado[1] have studied the adsorption of vapors of water, ethanol, acetic acid and ethyl acetate by thoria and alumina at 99.4°. They believe the most plausible explanation of catalytic esterification to be that "in the passage of the vapors of ethyl alcohol and acetic acid over alumina or thoria the alcohol molecule is strongly adsorbed, primarily through the residual valencies of the hydroxyl group. Under the prevailing conditions of stress the less highly attracted ethylidene group splits off from the alcohol molecule and there combines with the acid molecule to form the ester."

Bischoff and Adkins[2] measured the adsorption by three varieties of titania of certain products of the catalytic reactions in order "to discover the relationship that has been supposed to exist between the adsorptive power of substances and their catalytic activity," but find that "the adsorption measurements of the products of reaction at the surface of titania show no connection with either the activity of the catalyst or its selective effects." "It is important to note that the adsorbing powers of the three catalysts are not in the same order as their catalytic activity."

Bone and Andrew[3] find that the catalytic activity of a gold surface for the union of carbon monoxide and oxygen is increased by exposure to either gas. Both gases seem to be activated at the catalytic surface.

That the relation between adsorption and catalytic activity is not as simple as might be supposed appears from the observations of Remy and Gönningen[4] who studied the synthesis of water over the metals of the iron group and ruthenium and their alloys. Previous treatment with oxygen makes iron alloys more active, while hydrogen increases the activity of nickel alloys; but pure iron and iron-ruthenium alloys are less active after treatment with oxygen.

Veil[5] finds that certain metallic hydroxides alter their magnetic properties progressively while catalyzing the decomposition of hydrogen peroxide. Boswell and Bayley[6] consider the normal platinum catalyst to consist of particles of platinum with interior content of oxygen, the particles being surrounded by a layer of dissociated water, the hydrogen and hydroxyl ions alternating. This layer they believe to be the seat of the catalytic action. A nickel catalyst is similar.

Boswell and Dilworth[7] extend this idea to alumina. "All the above reactions catalysed by aluminium oxide involve the elements of water, and in

[1] J. Phys. Chem., **29**, 256 (1925).
[2] J. Am. Chem. Soc., **47**, 807 (1925).
[3] Proc. Roy. Soc., **109A**, 459 (1925).
[4] Z. anorg. allg. Chem., **149**, 283 (1925).
[5] Compt. rend., **182**, 1028 (1926).
[6] J. Phys. Chem., **29**, 11 (1925).
[7] J. Phys. Chem., **29**, 1489 (1925).

the two former either the addition or removal of water to or from the other reacting compound. Associated with this is the fact that aluminium oxide catalyst contains water, and the further fact that when this water content is diminished by heating at a high temperature the catalytic activity is likewise diminished. This all points to the conclusion that this catalyst functions by means of a surface film of water and that this film is the real seat of the catalysis. The marked stability of the film indicates that it is present in a special condition such as positively charged hydrogens and negatively charged hydroxyls, alternating with each other and completely enveloping each aluminum oxide particle.

"That is, the initiation of the reactions comes from the charged hydrogens and hydroxyls on the aluminium oxide particles. These react with the hydrogens or hydroxyls, or both, in the compounds brought in contact with the heated surfaces, thus setting up the reactions which always result in the formation of as much water as has been removed from the catalytic surface. The surface film is thus restored and the cycle continues.

"The catalyst from this point of view does not accelerate a reaction already in progress . . . but actually initiates the change. . . ."

Intermediate Compounds

There have been two extreme views as to the action of a catalyst. One, that the catalyst simply speeds up a reaction by its presence without taking any part in it. The other, that the catalyst is actually a reactant but is regenerated in the end. The latter view, or intermediate compound theory goes back to Desormes and Clement.[1] This has been strongly advocated by Sabatier all along and has been "the guiding star" in all of his investigations as he says in his book and in his address before the American Chemical Society.[2] He believes that the temporary hydrides NiH_4 and NiH_2 are formed and give their hydrogen to the organic compounds in catalytic hydrogenation.

Kubota and Yoshikawa[3] regard reduced nickel catalysts as containing many active unstable hydrides. They divide these into three classes, the first or most active being able to hydrogenate benzene and to be poisoned by thiophene. The second can reduce ethylenic groups and is poisoned by ethyl sulphide while the last is only able to reduce nitro-groups and is poisoned only by hydrogen sulphide. The same theory is promulgated by Mittasch[4]; but he is somewhat more liberal in his definition of compound. He feels that in homogeneous systems, particularly in solutions, there is no doubt that catalysis takes place by causing intermediate reactions. After enumerating the difficulties that stand in the way of exact measurements he says: "Yet it remains, according to my judgment, *that here also the intermediate reaction hypothesis is the most suggestive and most satisfactory explanation, provided one takes a broad enough view;* i.e., when it is taken into account that in addition to

[1] Ann. Chim. Phys., **59**, 329 (1806).
[2] Ind. Eng. Chem., **18**, 1005 (1926); Chem. Listy, **20**, 45 (1926).
[3] Sci. Papers Inst. Phys. Chem. Research, **3**, 223 (1925).
[4] Ber., **59**, 13B (1926).

the chemical processes with their velocities there are also physical processes with their own velocities." There is not always agreement among investigators as to the exact hypothetical intermediate processes involved in a catalytic reaction. As is known, some follow Sabatier in considering hydrogenation with nickel as more chemical, involving labile nickel hydride, possibly with the participation of oxygen (Schlenk, Willstätter, Waldschmidt), while others regard it as more of a physical process in which adsorption plays the leading role: "This adsorption may be simply physical, depending on capillarity and the critical constants of the gases, or may be specific and chemical involving valence forces."

Person[1] reviews the theories of catalysis from the standpoint of intermediate compounds. He finds it possible to approach catalytic reactions through the electron theory. Child and Adkins,[2] in a study of the condensation of an aldehyde to an ester, assume that an aldehyde-catalyst complex is formed rapidly and that this decomposes slowly into the ester and catalyst.

Duparc, Wenger and Urfer[3] regard catalytic oxidation in the presence of the metals of the platinum group as depending on the formation of oxides of these metals. "With platinum we see that the yields [of sulphur trioxide] are small while the metal is PtO, they increase suddenly when the platinum goes to the condition PtO_2, and they come down again [with rise of temperature] as the oxide begins to dissociate, till at 800° the yields are zero."

E. and F. Müller[4] suppose a series of intermediate compounds in the decomposition of formaldehyde by the metals of the palladium group. Benton and Emmett[5] conclude that the union of oxygen and hydrogen in contact with reduced nickel is accounted for by the alternate oxidation and reduction of the metal. Andrussov[6] postulates intermediate compounds in the catalytic oxidation of hydrocyanic acid and ammonia. Travers[7] assumes an intermediate complex in the oxidation of manganese.

Yost[8] supposes the trivalent silver ion to be the active agent in oxidation of ammonia by persulphates. Intermediate reactions are discussed by Rosenmund and Jordan[9] and by Gulevich[10] in the catalytic reaction of oximes. Rosenmund[11] assumes an intermediate complex in the formation of secondary amines. Euler, Olander and Rudberg[12] deduce formulae for velocity of the mutarotation of glucose from assumptions that glucose forms salts amphoteri-

[1] J. Russ. Phys.-Chem. Soc., **57**, 189 (1925).
[2] J. Am. Chem. Soc., **47**, 798 (1925).
[3] Helv. Chem. Acta., **8**, 609 (1925).
[4] Z. Elektrochemie, **31**, 41 (1925).
[5] J. Am. Chem. Soc., **48**, 632 (1926).
[6] Ber., **59**, 458 (1926).
[7] Compt. rend., **182**, 972 (1926).
[8] J. Am. Chem. Soc., **48**, 374 (1926).
[9] Ber., **58**, 51 (1925).
[10] Ber., **58**, 798 (1925).
[11] Z. angew. Chem., **38**, 145 (1925).
[12] Z. anorg. allg. Chem., **146**, 45 (1925).

cally. Euler and Olander[1] say: "Among the large number of catalyzed hydrolyses, not a single case is met with where it is objectionable to assume the formation of a salt between the catalyst and the reacting substances."

Spitalsky[2] develops equations for homogeneous catalysis on the basis of the formation of intermediate compounds between catalyst and reactant. All cases are thoroughly worked out and it is shown that the order of the reaction between catalyst and substrate may be entirely different from the apparent order of reaction deduced from the curve. The order of a catalyst reaction is determined by the affinity constant of the catalyst to the substrate so that a reaction of the nth order may run according to any order between o and n.

Merezhkorskii[3] regards variable valence as a prime requisite for a catalyst. "For a given reaction a catalyst is a body capable of modifying the valence of the reactants, able to combine reversibly with the reactants, at the same time having at least two stages of oxidation." Manchot and Gall[4] find that the platinum acts as hydrogen acceptor in the reversible dehydrogenation of hydroquinol. Job[5] explains a number of catalytic reactions by the formation of unstable electronic complexes which decompose, giving the final product of the reaction and regenerating the catalyst.

Two articles appeared practically simultaneously on the transformation of maleic into fumaric acid, by Meerwein and Weber[6] and Terry and Eichelberger.[7] In both, the assumption is made that the catalyst does not actually add to the double bond but only activates it. If one component of the double bond is disrupted there can be free rotation about the other. The latter authors believe the activation to be due to the addition of the catalyst to the unsaturated carboxyl groups. Lebeder, Koblinasky and Yabubchik[8] assume that hydrogenation depends on an unstable intermediate product (of the nature of an adsorption compound) between catalyst and unsaturated molecule.

Zelinskii[9] stresses the differences that must exist between the motions of particles in the surface and of those in the interior of an object. There are also peculiar conditions at the interface when two bodies touch. These may approach chemical phenomena which take place only on contact. He concludes: "The mechanism of catalysis does not demand the formation of intermediate compounds but is dependent upon the degree of tension of the chemical system, which tension is necessary for the initiation of chemical action and is brought about by the contact of bodies at ordinary or at elevated temperature.

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[1] Z. anorg. allg. Chem., **152**, 113 (1926).
[2] Z. physik. Chem., **122**, 257 (1926).
[3] Bull., (4) **39**, 41-3 (1926).
[4] Ber., **58**, 486 (1925).
[5] "Deuxième. Cons. Solvay," 417 (1926).
[6] Ber., **58**, 1266 (1925).
[7] J. Am. Chem. Soc., **47**, 1402 (1925).
[8] J. Chem. Soc., **127**, 417 (1925).
[9] Ber., **58**, 2755 (1925).

Alterations of the dynamic state of molecules during catalytic process are not doubted. These give the chief impulse to catalytic action." He quotes with approval Bodenstein's[1] statement that the formation of water from oxygen and hydrogen on a platinum surface concerns only the surface and that the adsorbed hydrogen is present not as hydride nor as atomic hydrogen but as *deformed hydrogen molecules.* The deformation results from the field of force on the surface of the catalyst which induces the adsorption and effects the deformation of the molecule." Partington[2] quotes Graham[3] as saying that the hydrogen molecule is adsorbed by one end and thereby polarized, the outer end having its affinity for oxygen increased.

Other chemists are outspoken in their opposition to the theory of intermediate compounds. Larson and Smith,[4] after a study of the catalytic synthesis of water, say: "With both nickel and copper the reaction was accompanied by the gradual formation of a stable oxide on the catalyst surface. This oxide decreased the catalytic activity of the metal."

Chapman, Ramsbottom and Trotman[5] studied the union of hydrogen and oxygen. They conclude: "Where silver is heated to dull redness in oxygen at a pressure exceeding 0.005 mm. of mercury, it becomes almost completely covered with a film of oxide, which considerably impairs the efficiency of the metal as a catalyst for the reaction between hydrogen and oxygen. The film of oxide can be removed by heating the metal to redness in a vacuum or in oxygen at a much lower pressure. The catalytic activity of the metal is then the same as that of silver which has been heated in hydrogen. These hypotheses furnish a consistent explanation of the discovery of Bone and Wheeler that silver, after it has been heated in hydrogen, becomes a much more efficient catalyst for the reaction between hydrogen and oxygen than silver which has not been thus treated. . . . The behaviour of gold is similar to that of silver . . . although . . . not so pronounced."

Bone and Andrew[6] investigated the union of carbon monoxide and oxygen over nickel and copper and their oxides. They conclude "that, in cases of surfaces composed either of readily oxidizable metals or reducible oxides, the true catalytic combination of the gases does not involve any alternating oxidation and reduction of the surface, as many have supposed; indeed, it was shown that any such purely chemical view is quite inadequate to explain the phenomenon. Thus, in the case of copper oxide, the truly catalytic process was shown to depend primarily upon the condensation of a film of "activated" oxygen on the surface; indeed, so far from the CuO participating directly in the formation of steam, it was actually protected by the film of "activated" oxygen from the attacks of the hydrogen, which otherwise would have energetically reduced it.

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[1] Ann., **440**, 177 (1924).
[2] Nature, **115**, 534 (1925).
[3] Proc. Roy. Soc., **16**, 422 (1868).
[4] J. Am. Chem. Soc., **47**, 346 (1925).
[5] Proc. Roy. Soc., **107A**, 92 (1925).
[6] Proc. Roy. Soc., **110A**, 16 (1926).

"The facts observed led to the conclusion that the real phenomenon of surface combustion "depends primarily on a condensation of one or other (*and in some cases, possibly both*) of the reacting gases on the heated surface," and that the prime cause is an "activation" of the combining gases (certainly of the hydrogen, and possibly also of the oxygen) by "association" with the surface, the question being left open whether such "association" is a mere surface "condensation" or some deeper "occlusion."

"The catalyzing power of the surface, when in "normal" activity, can be highly stimulated by previous exposure to *either* carbon monoxide *or* oxygen at the said experimental temperature; in neither case, however, was the full extent of such stimulus immediately manifested when the stimulating gas was rapidly removed and a fresh charge of the reacting mixture ($2CO+O_2$) re-introduced into the apparatus.

"Although the catalytic combustion was subsequently found to depend on the presence of moisture in the system, no hydrogen was ever detected in the reacting gases, even when a large excess of carbon monoxide was present.

"A microscopic examination of the gold surface, at the conclusion of the experiments failed to reveal any signs of "pitting" having occurred; on the contrary, neither the lustre nor the smoothness of the metal seemed to have suffered any diminution."

Böeseken[1] combats, with vigor and effect, the idea of intermediate compounds.

It has been shown that aluminum chloride combines with acid chlorides and this has been considered an explanation of the Friedel and Crafts reaction. It is here brought out that molecules such as chlorine, ethyl chloride, carbon tetrachloride, which either do not combine with aluminum chloride or do so with difficulty, react on aromatic hydrocarbons much more vigorously and with the aid of much less of the catalyst than the acid chlorides which form molecular compounds with the aluminum chloride. Benzyl chloride "does not give an addition product but reacts rapidly at 0° while its nitro derivative forms a well-crystallized addition product $NO_2C_3H_4CH_2Cl.AlCl_3$ which reacts with benzene but does so only at a higher temperature, *i.e., under the conditions under which the addition compound begins to dissociate.* The formation of addition products may inhibit the reaction entirely and we may conclude that the formation of addition products never gives a satisfactory explanation of catalytic action. If the catalyst and one of the reactants combine they usually do so with a liberation of energy which leaves the system with less energy than it had before. This means that a larger amount of energy will be required to start the reaction."

"The explanation of catalytic phenomena must be sought in what happens during the contact between the catalyst and the activated molecules. I assume that particular bonds are modified and I have called this *dislocation.* We can imagine that the catalyst without combining intimately with the bond which it is to activate, changes the orbits of the electrons in such a way that the molecule can act much more rapidly than without this change."

[1] Rec. Trav. chim., **45**, 458 (1926).

Carriers

Rosenmund and Joithe[1] think that the carrier plays a part in the reaction. In the reduction of borneol to iso-camphane, it has been assumed that the alumina caused water to split off and then the nickel effected hydrogenation. They consider that the splitting off of the water would be too slow at the low temperature and assume formation of complexes. "The borneol and H_2 are bound to the catalyst by partial affinities. This using up of the affinities on the outside weakens the internal bonds and prepares for a rearrangement of the forces. . . . The rôle of the alumina is a double one; in consequence of its powerful adsorptive power it binds the borneol to the catalyst, secondly it splits water from the labile complex and helps finish the process. The reduction process appears as condensation between ROH and H_2 in which the nickel loosens up the H_2 while the alumina aids the splitting off of the water. . . . The complex-theory of catalyst gains ground more and more as we have investigated it. Wieland,[2] who has formerly proposed complex-formation in certain reduction processes, now holds it,[3] as do we, of general application."

Modification of Catalysts

In promoted action and in negative catalysis we have a change in the velocity of a catalyzed reaction, here we have to do with a modification of the direction of the reaction. It is quite common that a catalyst facilitates two or more reactions as thoria dehydrates and also dehydrogenates an alcohol, the two reactions going on simultaneously. Adkins has shown that alumina prepared in different ways gives very different ratios of ethylene and hydrogen. If we add to a double-acting catalyst a selective promoter, one which will speed up the one of the reactions but not the other, almost the whole product will be that of the favored reaction.

Extremely important results have been obtained by Adams and his coworkers on the modification of the platinum oxide catalyst by the addition of various substances, particularly iron salts. The hydrogenation of a compound, such as citral or cinnamic aldehyde in which a double bond and an aldehyde group are present, can thus be directed so as to yield the unsaturated alcohol or the saturated aldehyde practically completely. For details of procedure and many examples reference is made to the papers of Carothers and Adams,[4] Kern, Shriner and Adams[5] and Adams and Garvey.[6] Faillebin[7] also has studied the modification of a platinum catalyst by the addition of iron and other substances. Komatsu and Kurata[8] have experimented with modified copper catalysts. Hara[9] prepared copper catalysts one of which was de-

[1] Ber., **58**, 205 (1925).
[2] Ber., **145**, 484 (1912).
[3] Ergeb. Physiol., **20**, 516 (1922).
[4] J. Am. Chem. Soc., **47**, 1047 (1925).
[5] J. Am. Chem. Soc., **47**, 1147 (1925).
[6] J. Am. Chem. Soc., **48**, 477 (1926).
[7] Ann. Chim., **4**, 156, 410 (1925); Compt. rend., **182**, 132 (1926).
[8] Mem. Coll. Sc. Kyoto, **8A**, 35, 147 (1925).
[9] Mem. Coll. Sc. Kyoto, **9A**, 405 (1926).

hydrating and another dehydrogenating. Komatsu and Masumoto[1] compared nickel, copper and thoria catalysts at different temperatures and found that the activity of thoria is most influenced by temperature.

Armstrong and Hilditch[2] investigated the various factors in selective hydrogenation particularly the relative location of the double bonds. Richardson and Snoddy[3] have studied the selectivity of platinum and nickel catalysts in the hydrogenation of oils containing more than one double bond. Rosenmund and Jordan[4] hydrogenated aromatic aldehydes. By partially poisoning the catalyst they were able to stop at the alcohol.

Zetzsche[5] with Arnd, Enderlin, Flutsch, Menzi, and Loosli as coworkers, has used partially poisoned or "regulated" catalysts for the hydrogenation of acid chlorides. According to Paal and Poetke[6] the action of palladium on formic acid is different according to whether the solution is acid or neutral. Galecki and Mlle. Bincer[7] and Galecki and Mlle. Krzeczkovska[8] have experimented with gold sols prepared in various ways and found great differences in their activities.

Promoters

Under this head are grouped a variety of phenomena. Tuly and Adams[9] find that zinc and iron salts are truly remarkable as promoters with the platinum oxide catalyst. In this way cinnamic acid can be hydrogenated to the corresponding alcohol without reactivation of the catalyst. Bray and Doss[10] show that a mixture of manganese dioxide and copper oxide is more efficient in the catalytic oxidation of carbon monoxide than either of these oxides alone.

Robertson[11] in a study of the decomposition of hydrogen peroxide by ferric and cupric salts and mixtures of these, defines promotion provisionally "as a change in the path of a reaction with a concomitant displacement of the steady state." The absorption spectra indicated the presence of cupric acid when ferric iron was promoted by copper. Quartaroli[12] has investigated the same reaction with the same two catalysts. The activity of cupric hydroxide is increased 50-fold by ferric hydroxide which alone is only slightly active. The most powerful catalyst is a mixture of the two in presence of alkali. He finds wide variations in the activity of catalysts according to the proportions of the reactants.

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[1] Mem. Coll. Sc. Kyoto, 9A, 15 (1926).
[2] Proc. Roy. Soc., 108A, 121 (1925).
[3] Ind. Eng. Chem., 18, 570 (1926).
[4] Ber., 58, 160 (1925).
[5] Helv. Chem. Acta, 8, 591 (1925); 9, 177, 182 (1926).
[6] Ber., 59, 1511 (1926).
[7] Bull. Acad. polonaise, 1925, A, 93.
[8] Bull. Acad. polonaise, 1925 A, 111.
[9] J. Am. Chem. Soc., 47, 306 (1925).
[10] J. Am. Chem. Soc., 48, 2060 (1926).
[11] J. Am. Chem. Soc., 47, 1299 (1925).
[12] Gazz., 55, 252, 619 (1925).

Russell and Taylor[1] observe that 10% of thoria increases the activity of a nickel catalyst ten times. "Therefore, it appears impossible to explain the action of the promoter either by a quantitative extension of surface, or by a change in the relative concentrations of the adsorbed reactants. It seems probable, however, that the surface of the promoted catalyst is such that it holds adsorbed in a reactive condition a larger fraction of the total amount of gas adsorbed than does the unpromoted catalyst."

Cassel[2] considers it necessary to assume that molecules absorbed on the gas-solid interface have two-dimensional heat motion. "Each of the two reacting gases is preferentially adsorbed on one of the two phases of the solid catalyst."

Käb[3] investigated the effect of gases on the activity of platinum in the decomposition of formic acid. Platinum prepared in high vacuum was found to be active. That saturated with hydrogen or carbon monoxide was inactive while that containing oxygen was moderately so. The catalyst could be reactivated by evacuation. "*The assumption made by many that platinum without oxygen is not able to effect the catalytic transfer of hydrogen is rendered improbable by this experiment. . . . The most active black appears to be one without any adsorbed gas.* A superficial adsorption of oxygen after disintegration appears to have only the advantage of avoiding loading with the harmful gases, hydrogen, carbon monoxide, etc., and to keep these away until the black enters the reaction; yet it is not necessary for catalytic action and is lost, as the following electromotive experiments show, immediately on contact with hydrogen."

Waldschmidt-Leitz and Seitz[4] maintain that *oxygen-containing and oxygen-free platinum black are* to be regarded as *two different catalysts* of which only the first is capable of adding hydrogen to unsaturated compounds. "The influence of the electrical force, emanating from the positive metal and acting in the intermediate layer, on the stability of the hydrogen molecule will make itself felt to different degrees according to the greater or less possession of the metal surface by oxygen; so the significance is seen of the dependence of the specific activation of hydrogen on the oxygen content of the catalyst, as has been observed in the hydrogenation of napthalene."

Kuhn[5] takes quite a different view of the action of oxygen. He assumes that: "In the interior of the platinum there are hydrogen nuclei and free electrons. As these leave the platinum the recombination begins passing through excited and normal hydrogen atoms, H_2 ions and excited H_2 molecules finally to the normal inactive H_2. The path of these various recombinations lies on the surface of the platinum and in its immediate vicinity where the substance to be hydrogenated is. On pure platinum and palladium the recombination is so catalyzed that only normal H_2 molecules reach the sub-

[1] J. Phys. Chem., **29**, 1325 (1925).
[2] Naturwiss., **14**, 103 (1926).
[3] Z. physik. Chem., **115**, 224 (1925).
[4] Ber., **58**, 563 (1925).
[5] Naturwiss., **13**, 169 (1925).

strate and no hydrogenation takes place." If the surface is poisoned by oxygen or air then active hydrogen reaches the substrate. The oxygen is a poison for the catalyst that would destroy the active atomic hydrogen on which the hydrogenation depends.

Schmidt[1] suggests that the presence of a second metal in a catalyst may serve as a promoter by preventing sintering which would diminish its activity. Wyckoff and Crittenden[2] made an X-ray examination of some ammonia catalysts. They find that the presence of potassium and aluminium oxides maintains a large iron surface by preventing the growth of iron crystals.

Stadnikov, Gavrilov and Vinogradov[3] observe that carbon deposited on finely divided iron is extraordinarily active in reductions at relatively low temperature. According to Rideal and Wright[4] nitrogen and iron have great influence on the catalytic power of charcoal in the oxidation of oxalic acid. "The incorporation of 10% of urea in sugar and activation of the resultant charcoal by slow combustion until some two-thirds have been removed by oxidation, will produce a charcoal of specific surface of 200 sq. in. per g. . . . The incorporation of these "promoters" in the carbon results in the extension of the total surface and possibly a small extension in the fraction of the surface which is catalytically active. At the same time, two new types of catalytically active surface make their appearance: an iron-carbon-nitrogen complex surface with a specific activity some 800 times that of the original active-carbon surface, and an iron-carbon surface with a specific activity some 50 times that of the original surface." Sandonnini[5] has found that carbon is a more active catalyst with copper and that the effect of the two is moderately increased by light.

Chirnoaga[6] observes that alumina is without action in the decomposition of sodium hypochlorite but that it is a promoter for nickel and cobalt peroxides. Mixtures of these two oxides are more effective than either alone, the maximum being at 30% nickel.

Medreder[7] has studied the catalytic oxidation of methane with free oxygen and finds that the addition of 4% of hydrogen chloride raised the precentage of methane oxidised from 2 to 27°. With a small amount of hydrogen chloride, formaldehyde is the chief product but much causes the formation of carbon monoxide. The best yield of formaldehyde was with a mixture of the phosphates of tin, iron and aluminium as catalyst and 0.13% hydrogen chloride.

Taipale[8] observes that the nature of the solvent has much influence on the rate of hydrogenation of amines, acetic acid being the best solvent, ether, methanol and ethanol being poorer.

[1] Z. physik. Chem., **118**, 193 (1925).
[2] J. Am. Chem. Soc., **47**, 2866 (1925).
[3] Ber., **58**, 242 (1925).
[4] J. Am. Chem. Soc., **1926**, 1813.
[5] Atti Accad. Lincei, (6) **2**, 427 (1925).
[6] J. Chem. Soc., **1926**, 1693.
[7] Trans. Karpov Inst. Chem., **1925**, No. 4, 117.
[8] J. Russ. Phys.-Chem. Soc., **57**, 487 (1925).

Taylor and Close[1] have studied the acid catalysis of lactone formation. The reaction is much faster in wet ether than in dry. This looks like a case of the influence of water but they believe that the velocity is not dependent on the solvent but depends "upon the thermodynamic activity of the hydrogen ion which may correspond to the concentration of the unhydrated ion."

Abderhalden and Komm[2] have investigated the oxidation of glycine anhydride by hydrogen peroxide under the action of sunlight aided by ferrous sulphate. The effect of hydrogen ion concentration has been shown by Witzemann[3] who finds that the oxidation of butyric acid by hydrogen peroxide is slower in presence of monosodium phosphate than with the disodium salt.

Clark, McGrath and Johnson[4] have studied the effect of X-rays on the catalytic oxidation of sulphur dioxide. They find no effect in dry air but a slight increase of oxidation in presence of moisture.

Smith[5] has found the effect of gum arabic and other colloids on the rate of hydrolysis of esters in heterogeneous systems to be quite irregular sometimes in one direction and sometimes in the other. In homogeneous systems the effects were slight. Brönsted and King[6] have investigated salt effects in hydroxyl ion catalysis.

Induced Reactions. These may be considered cases of catalysis provided we are not strict in holding to the idea that the catalyst suffers no change. Reference must be made to the admirable review of oxidation catalysis by Moureu and Dufraisse[7] for much material that can not be discussed here.

Dey and Dhar[8] oxidise sulphur, sugars, starch and various other substances by passing air at room temperature into solutions containing these and finely divided copper, cuprous chloride or oxide or yellow phosphorus. They regard induced reactions as due to activation by emitted ions. Palit and Dhar[9] add a number of observations on the oxidations of carbohydrates in presence of ferrous hydroxide and sodium sulphite. They find that "substances which are difficultly oxidised by passing air can be usually more readily oxidised in presence of reducing agents than in presence of a feeble oxidising agent like ferric salt or cupric salt." According to Spoehr and Smith[10] sodium ferropyrophosphate which is itself readily oxidised by air is a catalyst for the air oxidation of carbohydrates and hydroxy acids by air.

Horiuchi[11] finds that safrol is isomerized by heating with 20% caustic potash at 180°-200°. Eugenol is not affected by this treatment when alone but is isomerized if mixed with safrol. With 15% alkali at 160°-170° neither is changed when alone, but both are if they are mixed together.

[1] J. Phys. Chem., **29**, 1085 (1925).
[2] Z. physiol. Chem., **144**, 234 (1925).
[3] J. Am. Chem. Soc., **48**, 202 (1926).
[4] Proc. Nat. Acad. Sci., **11**, 646 (1925).
[5] J. Chem. Soc., **127**, 2625 (1925).
[6] J. Am. Chem. Soc., **47**, 2523 (1925).
[7] Chem. Rev., **3**, 113 (1926).
[8] Z. anorg. allg. Ch., **144**, 307 (1925).
[9] J. Phys. Chem., **30**, 939 (1926).
[10] J. Am. Chem. Soc., **48**, 236 (1926).
[11] J. Chem. Soc. Japan, **45**, 209 (1925).

Catalyst Poisons and Negative Catalysts

Maxted[1] finds that the adsorption of lead and mercury ions by a platinum catalyst is linear up to saturation. So is the poisoning curve. "Thus the activity of the catalyst in the presence of such a poison is, at any rate for the first stage, a linear function of the actual concentration of poison on the surface of the catalyst." He restricts poisoning to heterogeneous systems as he can see no meaning to this word when applied to a homogeneous system.

Kubota and Yoshikawa[2] have studied the toxicity of thiophene for nickel and copper catalysts. Nickel is rapidly poisoned at 300° by 1% of thiophene in benzene yet its activity for hydrogenating phorone was maintained. The rapidity with which nickel is poisoned depends on the temperature at which it is reduced, the higher the temperature, the more rapid the poisoning. Copper is not affected by thiophene.

Boswell and Bayley[3] consider the normal platinum or nickel catalyst to consist of particles of the metal with interior content of oxygen, the particles being surrounded by a layer of dissociated water, this layer being the seat of catalytic oxidation and reduction. They say: "Experiments on the poisoning of nickel and platinum catalysts by chlorine seem to indicate that the poisoning is accomplished by the destruction of the surface film on the catalytic particles, which film is the seat of the normal catalytic action, thus rendering the interior oxygen content accessible to free hydrogen. This interior oxygen so vital to the maintenance of this surface film and hence of catalytic action in the normal catalyst, is thus quickly removed."

Bakj[4] has investigated the poisoning of palladium catalysts for the reaction:— $NaH_2PO_2 + H_2O \rightarrow NaH_2PO_3 + H_2$.
He thinks the poisoning to be due partly to chemical combination with the palladous chloride and partly to adsorption on the palladium black. For 1 atom of palladium, 1.75 molecules of potassium cyanide, 1 of mercuric chloride, 1.5 of thiourea and more than 10 of quinine hydrochloride were required.

Charrion[5] dehydrated alcohol at 250° with alumina containing various additions. Calcium oxide, phosphoric acid, cobalt and copper oxides, tungsten trioxide and sulphuric acid and mercury inhibit the reaction in the order given.

Wieland and Fischer[6] have found a curious case. The rate of oxidation of oxalic acid by hydriodic acid is reduced 88% by 0.0001 mole. hydrocyanic acid and is stopped by twice this amount. They regard the hydrocyanic acid as an anticatalyst but the most painstaking search failed to reveal the catalyst.

Quartaroli[7] observes that one part of hydrogen peroxide in 200,000,000 parts of water can be detected by its effect on the color change of cupric hy-

[1] J. Chem. Soc., **127**, 73 (1925); Ind. Chemist, 1, 449 (1925).
[2] Sci. Papers Inst. Phys. Chem. Res. (Japan), **3**, 33 (1925).
[3] J. Phys. Chem., **29**, 11 (1925).
[4] Trans. Karpov. Inst. Chem. (Russia), **1925**, No. 4, 11.
[5] Compt. rend., **180**, 213 (1925).
[6] Ber., **59**, 1171 (1926).
[7] Gazz., **55**, 264, (1925).

droxide. This reaction is hindered by salts of magnesium and other electrolytes even in extremely small amounts. Zetzsche and Arnd[1] have investigated the purification of solvents used in hydrogenation. Lamb and Vail[2] have made an elaborate study of the effects of different amounts of moisture on Hopcalite and "conclude that the activity of the catalyst is primarily determined by its water content." Constable[3] finds that the temperature coefficient for the dehydrogenation of alcohol remains the same during gradual poisoning.

Cusmano[4] concludes that camphor does not act as a contact catalyst in the union of sulphur dioxide and chlorine but rather by virtue of the residual valence of its oxygen. Organic compounds containing the groups $=CO$, $-CO_2H$ or $-O-$ act as positive catalysts for this reaction but those containing the groups $-NO_2$, $-SO_2H$ or a halogen inhibit the reaction.

Goldschmidt and Mathiesen[5] have made a comparison of the catalytic action and the conductivities of hydrochloric, hydrobromic and hydriodic acids in butyl alcohol and find water to be an anti-catalyst. Toda[6] observed the oxidation of cystein by methylene blue. This reaction is inhibited by hydrocyanic acid from which it is supposed to be due to an unknown catalyst. It is speeded up by a trace of iron. Palit and Dhar[7] dissolved metals in nitric acid in presence of catalysts. Reducing agents, except formic acid, retard the solution.

According to Gault and Trauffault[8] chloroform is readily chlorinated without a catalyst but this is prevented by ferric chloride.

The subject of catalysis and auto-oxidation is handled so extensively and in in such a masterly way by Moureu and Dufraisse[9] that it need not be treated here except for a few references.

Moureu, Dufraisse and Lotte[10] find that "practically all catalyzers of auto-oxidation (either positive or negative) are easily oxidisable substances." They usually contain hydroxyl, iodine or sulphur. Methoxyl is inactive. Sulphones and sulphoxides are inactive.

Moureu and Dufraisse[11] regard catalytic oxidation as dependent on the formation of a sort of peroxide. "The antioxygens act by decomposing catalytically the peroxide A $[O_2]$ which results from the union of the auto-oxidisable substance with a molecule of free oxygen." In a later article[12] they find nitrogen compounds to be important.

[1] Helv. Chem. Acta, 9, 173 (1926).
[2] J. Am. Chem. Soc., **47**, 123 (1925).
[3] Proc. Camb. Phil. Soc., 22, 738 (1925).
[4] Gazz., **55**, 218 (1925).
[5] Z. physik. Chem., **121**, 153 (1926).
[6] Biochem. Z., **172**, (1926).
[7] J. Phys. Chem., **30**, 1125 (1926).
[8] Compt. rend., **179**, 467 (1924).
[9] Chem. Rev., **3**, 113 (1926); "Deuxième Cons. Solvay," 524 (1926).
[10] Compt. rend., **180**, 993 (1925).
[11] J. Chem. Soc., **127**, 1 (1925).
[12] Compt. rend., **182**, 949 (1926).

Dhar[1] combats Luther's view[2] that a negative catalyst only counteracts a positive. He maintains that negative catalysts are much more numerous than positive. The most of the substances that hinder oxidation are reducing agents. "It is very probable that the phenomena of negative catalysts of induced reactions and of formation of molecular complexes are in close relation to each other."

Underwood[3] follows Taylor's theory that inhibitors function by forming molecular compounds with the active molecules of the substance which is being preserved. The stabilizing actions of 25 substances towards chloroform were studied without finding serious disagreement with this theory. Fugitive dyes may be protected against fading in light by treatment with a solution of phenol or resorcinol. Granting that the active molecules are thus taken care of, the question arises why are new active molecules not formed? They naturally would be if the assumption is correct that, under given conditions, a certain portion of the molecules is active.

Over a hundred inhibiting agents for the oxidation of oils have been studied by Smith and Wood[4]. "The most effective are basic unsaturated compounds as the amines, aromatic phenols, and inorganic basic reducers." They conclude that:

1. "The antioxidant being basic, combines with the acidic products of oxidation and prevents them from acting as auto-catalysts toward oxidation.
2. "The triple-bonded nitrogen atom with two partial valencies or elements with free valences forms intermediate compounds with the easily oxidised ethenoid carbon.
3. "This temporary compound controls the rate of reaction for a definite, but limited period of time."

Observations on Catalysis

Under this head are noted numerous investigations in which the theory of catalysis is not the prominent part. They contain a host of observations of catalytic effects of many classes. On account of their number little space can be given to any one.

Dehydration. Adkins and Perkins, Lazier and Adkins, Adkins and Lazier[5] have made a comprehensive study of the dehydration and dehydrogenation of alcohols over alumina and zinc oxide. Bonham[6] and Kesting[7] have passed propyl and ethyl alcohol over alumina, clay, etc. Clark, Graham and Winter[8], and Jatkar and Watson[9] have found alumina and alum to be excellent catalysts for the preparation of ether from the alcohols, while Plüss[10] has used

[1] Z. anorg. allg. Chem., **144**, 289 (1925).
[2] Z. physik. Chem., **45**, 662 (1903).
[3] Proc. Nat. Acad. Sci., **11**, 78 (1925).
[4] Ind. Eng. Chem., **18**, 691 (1926).
[5] J. Am. Chem. Soc., **47**, 1163 (1925); **47**, 1719 (1925); **48**, 1671 (1926).
[6] J. Am. Pharm. Asso., **14**, 114 (1925).
[7] Z. angew. Chem., **38**, 362 (1925).
[8] J. Am. Chem. Soc., **47**, 2748 (1925).
[9] J. Soc. Chem. Ind., **45**, 23, 1681 (1926).
[10] Helv. Chem. Acta, **8**, 507 (1925).

mixtures of alcohols. Takagi and Ishimasa[1] demethylate veratrol over a Japanese clay, lead sulphate and alum. Mailhe[2] decomposes the esters of secondary alcohols over alumina, thoria and titania.

Senderens[3] has made a comprehensive study of the preparation of ethers from both primary and secondary alcohols by heating the alcohols with sulphuric acid containing some water. The amounts of acid required decrease from 100% by volume for ethyl to 30% for heptyl. Less sulphuric acid is required for secondary. The temperatures used are from 100° to 145°. Excellent yields were obtained.

Darrell[4] finds 300° to be the optimum temperature for the preparation of ethyl amine from alcohol and ammonia over alumina. The influence of other factors was studied. Cleminson and Briscoe[5] show that the reaction, $2CO \rightarrow CO_2 + C$, does not take place below 300° in clean glass but does as low as 250° in presence of magnesia and alumina.

Hydrogenation and dehydrogenation. Pierce and Adams, Heckel and Adams, and Hiers and Adams[6] have applied hydrogenation with platinum oxide catalyst to various substances. The last article is a comparison of the oxide catalyst with colloidal platinum. Zelinskii and Turowa-Pollak[7] have compared the activity of platinum, iridium, rhodium, ruthenium, palladium and nickel for the hydrogenation of benzene at 7 temperatures, 100° to 300°. Negoshi[8] has determined the optimum conditions for the hydrogenation of acetaldehyde with nickel. Kluyrer and Douker[9] have studied the catalytic transfer of hydrogen. Ryerson and Thomas[10] have hydrogenated ethylene and phenol with palladium and nickel in silica gel. Nash[11] has prepared cobalt, copper and manganese catalysts for the hydrogenation of carbon monoxide. Carothers and Jones[12] prepared primary amines by the hydrogenation of nitriles with platinum. Chakravarty and Ghosh[13] used nickel on sugar charcoal in the hydrogenation of carbon monoxide. For this reaction at 300°, Franz Fischer, Tropsch and Dilthey[14] arrange the catalysts in this order: ruthenium, iridium, rhodium, nickel, cobalt, osmium, platinum, iron, molybdenum, palladium and silver. Zetzsche and Zala[15] dehydrogenated alcohols in the presence of cupric and cuprous oxides and manganese dioxide. Ghosh and Chakravarty have redetermined the equilibria: $H_2+HCHO \leftrightarrows CH_3OH$ and HCHO

[1] J. Pharm. Soc. Japan, No. **517**, 266 (1925).
[2] Caoutchouc and Guttapercha, **22**, 12937 (1925).
[3] Compt. rend., **180**, 790 (1925); **181**, 698 (1925); **182**, 612 (1926).
[4] J. Chem. Soc., **127**, 2399 (1926).
[5] J. Chem. Soc., **1926**, 2148.
[6] J. Am. Chem. Soc., **47**, 1098 (1925); **47**, 1712 (1925); Ber., **59**, 162 (1926).
[7] Ber., **58**, 1298 (1925).
[8] Report Osaka Ind. Res. Lab. Japan, **5**, No. 6, 1 (1924).
[9] Proc. Acad. Sci. Amsterdam, **28**, 605 (1925).
[10] "Third Colloid Symposium," **99** (1925).
[11] "Fuel in Science and Practice," **5**, 263 (1926).
[12] J. Am. Chem. Soc., **47**, 305 (1925).
[13] Quarterly J. Ind. Chem. Soc., **1**, 150 (1925).
[14] Brennst. Chem., **6**, 265 (1925).
[15] Helv. Chem. Acta, **9**, 288 (1926).

$\leftrightharpoons CO + H$[1] and obtained values different from the accepted. Escourron[2] discusses hydrogenation under reduced pressure. Komatsu and Tanaka[3] hydrogenated aniline over copper and nickel. The transfer of hydrogen from one part of a molecule to another is effected by nickel or copper according to Delaby and Dumoulin.[4] Vinyl-alkyl carbinols are thus transformed into ethyl ketones. Nickel is used by Mailhe[5] to decompose acid chlorides. Alkenes, carbon monoxide and hydrogen chloride are produced. Benzoyl chloride gives chlor-benzene and carbon monoxide.

Oxidation. Sinozaki and Hara[6] oxidised hydrocyanic acid to nitric oxide over a variety of catalysts. They believe cyanic acid to be first formed. Horiuchi and Uyeda[7] find that the nitrates of mercury and lead improve the yield in the oxidation of anethol to anisaldehyde. Lang[8] observes the accelerating effect of iodine and iodides on the oxidation of arsenious acid by permanganate. In the titration of oxalic acid with permanganate, Ridley[9] believes that both manganese ions and manganese sulphate molecules have catalytic effect.

Miscellaneous. Briner, Plüss and Paillard[10] obtained hexamethyl-benzene from phenol, etc., and methanol over alumina at 400°. Wibaut, Diekmann and Rutgers[11] find bismuth chloride to be a catalyst for the addition of hydrobromic and hydrochloric acids to ethylene and propylene. Tzentnershver and Straumanis[12] observed an increase in the rate of solution of zinc in mineral acids in the presence of various salts. Stadnikov and Ivanovskii[13] decompose fatty acids over iron at 400°. Yamaguchi[14] used reduced copper in Beckmann's rearrangement. The same author[15] tried the action of the same catalyst on pinacols. Koraczynski and Kierzek[16] find nickel, cobalt and copper powders and cobalt and nickel chlorides to be catalysts for indol synthesis.

The formation of acetals is comprehensively studied by Adams and Adkins.[17] Ferric and calcium chlorides were used. To be a catalyst the salt must form an alcoholate. The useful salts have acid reaction but the evidence is against catalysis by the hydrogen ion. Hara and Komatsu[18] pass an alcohol

[1] Quarterly J. Ind. Chem. Soc., **2**, 142 (1925).
[2] "Parfums de France," No. 26, 86 (1925.)
[3] Mem. Coll. Sc. Kyoto, **8A**, 135 (1925).
[4] Compt. rend., **180**, 1277 (1925).
[5] Compt. rend., **180**, 111 (1925).
[6] Tech. Rep. Tohoku I. U., **6**, 95 (1926).
[7] J. Chem. Soc. Japan, **45**, 203 (1924).
[8] Z. anorg. allg. Chem., **152**, 197 (1926).
[9] Chem., News, **130**, 305 (1925).
[10] Helv. Acta. Chem., **7**, 1046 (1924).
[11] Proc. Acad. Sci. Amsterdam, **27**, 671 (1924).
[12] Z. physik. Chem., **118**, 415 (1925).
[13] Trans. Karpov Inst. Chem. (Moscow), **1925**, No. 4, 175.
[14] Mem. Coll. Sc. Kyoto, **9A**, 33 (1925).
[15] Bull. Chem. Soc. Japan, **1**, 64 (1926).
[16] Gazz., **55**, 361 (1925).
[17] J. Am. Chem. Soc., **47**, 1358 (1925).
[18] Mem. Coll. Sci. Kyoto, **8A**, 241 (1925).

and ammonia over copper at 300° and get a nitrile. Mailhe[1] decomposes anides at 400° over nickel, nitriles being formed in some cases. Oparina[2] condensed isovaleric aldehyde with ammonia over alumina at 360° and obtained pyridine derivatives. Ipatiev and Klinkvin[3] condensed ethylene in an iron vessel with alumina. O. and C. A. Silberrad and Parke[4] have chlorinated toluene with several agents in presence of a large number of catalysts which they have classified. Nelson and Engelder[5] and Westcott and Engelder have decomposed formic acid by passing over copper, alumina, thoria and nickel at various temperatures from 350° up. Simons[6] has determined the decomposition products of triacetin and tripropionin over thoria at 500°. Blumbergn[7] has studied the decomposition of diazo compounds by copper, Paal and Boeters[8] have perfected the preparation of collodial cobalt. The sulphonation of anthraquinone in presence of mercury has been thoroughly investigated by Coppens.[9] Zelinskii[10] has shown that l-pinene passed over palladium asbestos gives a mixture of cymene and dihydropinene which shows that change of structure may be effected by a hydrogenation catalyst.

Richter and Wolf[11] isomerize beta pinene to the alpha by shaking with palladium containing hydrogen. If the metal does not contain hydrogen there is no change. According to Favorsky and Mlle. Chilingaren[12] certain ketones are isomerized by zinc chloride at 350°. Veil[13] has found that the activity of nickel hydroxide in the decomposition of hydrogen peroxide changes greatly with time and use. The magnetic properties were roughly parallel to the catalytic activity.

The following five papers pertain to homogeneous solutions. Livingstone and Bray[14] have studied the chlorine-chloride decomposition of hydrogen peroxide. Hammick, Hutchinson and Snell find the rate of oxidation of formic acid by bromine to be inversely proportional to the concentration of the hydrogen ion. The reaction is between the formate ion and molecular bromine. Euler and Olander[15] have investigated the splitting of acetoacetic ester by acids and bases and find that the rates are not proportional to hydrogen and hydroxyl ions. Brönsted and Duus[16] have used this reaction to

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[1] Bull., **37**, 1394 (1925).
[2] J. Russ. Physik. Chem. Soc., **57**, 319 (1925).
[3] Khim. Promushlennost', **3**, 57 (1925).
[4] J. Chem. Soc., **127**, 1724 (1925).
[5] J. Phys. Chem. **30**, 470, 476 (1926).
[6] J. Am. Chem. Soc., **48**, 1991 (1926).
[7] Chem. Weekblad., **22**, 599 (1925).
[8] Ber., **58**, 1542 (1925).
[9] Rec. Trav. chim., **44**, 907 (1925).
[10] Ber., **58**, 864 (1925).
[11] Ber., 59, 1733 (1925).
[12] Compt. rend., **182**, 221 (1926).
[13] Compt. rend., 180, 932 (1925).
[14] J. Am. Chem. Soc., **47**, 2069 (1925).
[15] Z. anorg. allg. Chem., **147**, 295 (1925).
[16] Z. physik. Chem., **117**, 299 (1925).

estimate the concentration of the base present. Kilpatrick[1] has carried on reactions in buffer solutions, and discussed salt effect.

As compared with the multitude of studies in which the regulation inorganic catalysts appear we have far too few investigations that involve organic catalysts. This is all the more true when we consider that the bodily functions of animals, growth and decay are probably initiated and regulated by organic substances which may be classed as catalysts. Morgulis, Beber and Rabkin[2] find catalase to be most active in the decomposition of hydrogen peroxide between 0 and 10°. According to Watson[3] the acid bromide is a powerful catalyst in the bromination of an aliphatic acid. Krasonskii and Kiprinov[4] condense phenyl-acetylene to *s*-triphenylbenzene using a primary amine as catalyst. Secondary and tertiary do not cause this reaction.

[1] J. Am. Chem. Soc., **48**, 2091 (1926).
[2] J. Biol. Chem., **68**, 521 (1926).
[3] J. Chem. Soc., **127**, 2067 (1925).
[4] J. Russ. Phys. Chem. Soc., **56**, 1, (1925).

SOCIETE DE CHIMIE INDUSTRIELLE
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ANNULE

LIGHT SCATTERING OF AQUEOUS SALT SOLUTIONS

BY C. W. SWEITZER*

Introduction

The only previous papers published on light scattering of aqueous salt solutions are two papers by R. Gans[1] and three preliminary notes by the author.[2] In Gans' papers measurements of the depolarization factor of an 18% sodium chloride solution, filtered through a collodion membrane, are given.

In the author's first preliminary note the results were inaccurate, on account of the lack of a sufficiently intense source of light, and because the scattered light contained fluorescent light, a fact which was not recognized at the time.

In the second preliminary note some of the calculated values of the scattering are different from the values given in the present paper. These differences are due, partly to more accurate values of ρ^3 in the present paper, partly to the greater accuracy used in the interpolation of μ^2 and partly to the differences in the values of the term $\partial p_2/\partial k$, which in this paper were determined from Tammann's values of vapour-pressure at 100°C., while previously they had been determined from Emden's values at 20°C.

Technique

Dust-free Salt Solutions.

Of the several methods for preparing dust-free liquids, *distillation in vacuo without ebullition* is impossible in the case of salt solutions of non-volatile salts. *Cataphoresis* is only possible in badly conducting liquids. *Ultrafiltration* through various filters has been tried in this laboratory by different experimenters including the author, but without success in the case of water and salt solutions; quantitative measurements of the light scattering always gave values higher than those obtained with solutions prepared dust-free by the envelopment method. *Centrifuging* has been tried in this laboratory, using a Sharples 30,000 r.p.m. centrifuge, but without success. The only other method available is that of *Envelopment* by precipitates. This method has been employed successfully for obtaining dust-free water by Spring[4] and Martin[5] but has never been used for any other than very dilute solutions, or for accurate comparative measurements in which the use of cross-shaped containers and parallel light is essential. The method used in

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[1] Z. Physik, **17**, 353 (1923); **22**, 44 (1924).

[2] Trans. Roy. Soc. Canada, **18**, 125 (1924); **19**, 31 (1925); **20**, 437 (1926).

[3] For meaning of these symbols see pp. 1159-1160.

[4] Rec. Trav. chim., **18**, 153, 233 (1899).

[5] J. Phys. Chem., **24**, 478 (1920).

this work for preparing all dust-free salt solutions (except the acids) was that of envelopment, using aluminium hydroxide for the majority of the solutions, cadmium hydroxide for the potassium iodide solutions, lead sulphate for the lead nitrate solutions and barium sulphate for the barium chloride solutions.

The *nature of the precipitate* did not influence the amount of scattering although aluminium hydroxide was preferable because it acted most rapidly in clearing the solutions and was accordingly used whenever possible. The time necessary for this clearing action varied with the nature of the precipitate and the concentration and nature of the solute. The minimum time in the case of the aluminium hydroxide was two weeks. The solutions of lead nitrate and barium chloride, where lead sulphate and barium sulphate were used respectively as the precipitates, took from four to six months to clear, depending on the concentration of the solution. Lead acetate solutions (not yet measured), with lead sulphate as the precipitate, have stood for over six months without becoming entirely dust-free. It was also found that a slight excess (10%) of either component used in the preparation of the precipitate had no measurable effect on the scattering. The weight of aluminium hydroxide that gave the best results was about 2.5 g. per litre of solution, this leaving approximately 2/3 of the solution free of precipitate.

Disinfectants: In some of the first solutions prepared formations were noticed which bore resemblances to bacterial growths. Consequently, small amounts of either mercuric chloride or chlorine were added to all the solutions, such additions having been found to have no measurable effect on the light scattering.

The nature of the containers: Winchesters were first tried, but as they showed traces of etching after several months, they were discarded. Erlenmeyer flasks of Pyrex showed no traces of etching and were used throughout this work. The length of time during which the solutions remained in the Pyrex containers had no measurable effect on the scattering values: Two identical 25% solutions of sodium chloride prepared in 1923 and 1925 gave scattering values ($H_2O = 1$) of 1.58 and 1.60 respectively when measured in 1925. Similar checks were obtained with an 18% sodium chloride solution and a 26% ammonium chloride solution.

The details of the preparation of the 26% ammonium chloride solution (prepared in 13/4/25) are given to illustrate the procedure followed in all cases.

180 g. Baker's C.P. aluminium chloride crystals were made up to 500 cc. with water, giving a 19.91% solution of anhydrous aluminium chloride. Three litres of about 26% Kahlbaum's ammonium chloride solution was similarly prepared. To 100 cc. of this ammonium chloride solution a measured quantity (about 5 cc.) of conc. ammonia (Baker's C.P.) was added. The approximately equivalent amount of aluminium chloride solution was then found by titration, using methyl orange as a rough indicator, and the final adjustment made by repeated filtering of small amounts and then testing for complete precipitation.

Aluminium chloride solution and ammonia, in the relative amounts found as above, sufficient to produce about 5 g. of precipitate, were added to a 2-litre Pyrex flask containing about 2 litres of ammonium chloride solution. Thus:

1925 cc. of the ammonium chloride solution,
10 cc. of chlorine water containing 0.04 g. chlorine,
48 cc. of the aluminium chloride solution,
15 cc. of concentrated ammonia

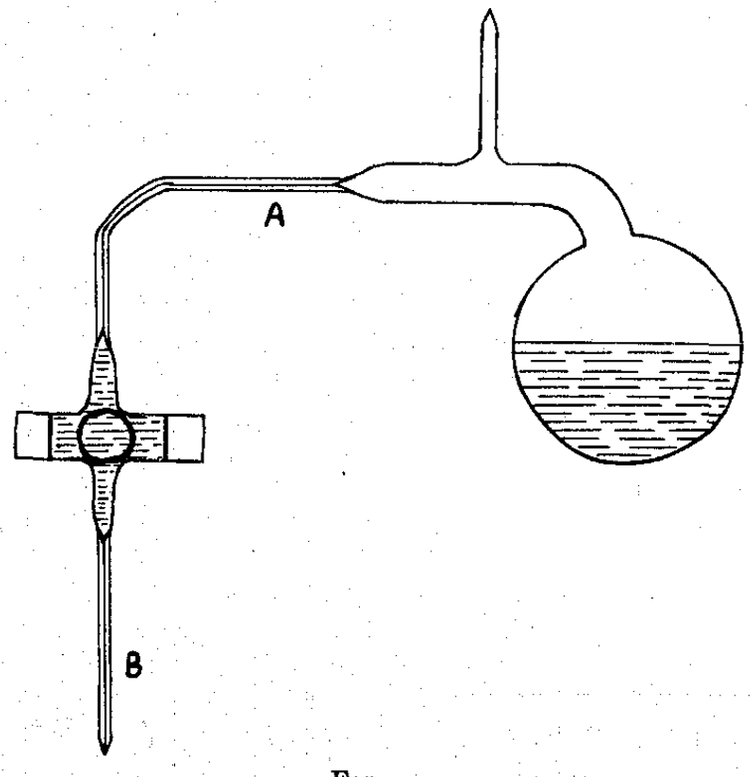


FIG. 1

were added to the flask in the order given. The flask was then well corked, shaken, labelled and left undisturbed. Several weeks later the solution was tested for dust by passing a convergent beam from a portable arc through the Erlenmeyer flask in a darkened room and examining the liquid at the focus with a lens. This test was repeated at intervals until the solution was found to be dust-free.

All the solutions measured (except the acids) were obtained dust-free by following a procedure similar to that above. For each set of salt solutions described later the recipe actually used for one particular concentration is given, the other solutions in that set being made by a similar recipe. Any variations from the above procedure will be indicated.

Transference to Crosses: Pyrex crosses from 20 to 25 mm. inside diameter for the arms, with capillary tubing attached as shown in Fig. 1, were constructed. The sealed-in plates of the crosses were cut from Pyrex plate No. G-702-E.J., obtained from the Corning Glass Company; these plates were first ground flat and polished by an Optical Company. The crosses withstood immersion in liquid air, and were also used as condensers for boiling

sulphuric acid without showing any signs of cracking. The cross was then sealed to a distillation flask (Fig. 1) and completely filled with dust-free water by the distillation in vacuo method.

The system was then broken at A and closed temporarily by rubber tube and clamp. A cork to fit the Erlenmeyer flask containing the dust-free solution was placed on the lower capillary, which was then broken at B. The open end was immediately immersed in the dust-free solution, so that the end B was about 2 in. above the precipitate (Fig. 2). The whole was allowed to

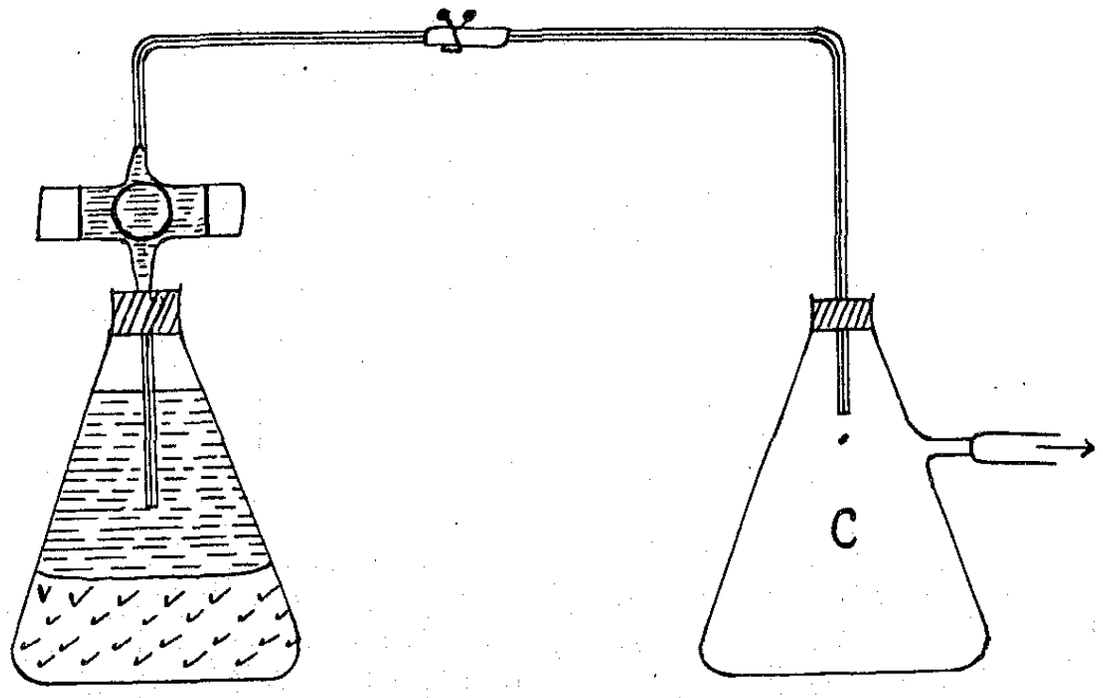


FIG. 2

stand overnight to permit any disturbed motes to settle. The suction flask C was then attached and the solution drawn up into the cross by a slight suction. The dust-free water was displaced by the salt solution which eventually filled the cross. Permanent seals in the capillary were made on both sides of the cross which was then ready to be used for the actual measurements.

Dust-freeness was always determined by a close examination of the liquid in the cross with a lens at the focus of an intense arc beam to see if any motes were visible; further, this focused light was examined from an angle of about 5° to the incident beam (towards the arc) to see if the scattered light had changed its shade (presence of larger motes would change the shade of the blue when viewed from here, compared with that seen at right angles). These two tests would always detect any motes in the liquid.

Apparatus for measuring the relative intensity of the scattered light.

On account of the very weak light scattering in most aqueous salt solutions an especially strong source of incident light was necessary. In the ap-

paratus described below in some detail and shown in Fig. 3, there is a departure from the Martin[1] method in the method of obtaining the comparison beam.

A is a high intensity carbon arc. The upper carbon contained a core of cerium oxide; these carbons were supplied by the Canadian National Carbon Company. A 50 amp. 110 volt D.C. was used. The arc was placed in an asbestos-lined box, and a stove-pipe connection to the ventilator shaft was used to carry off the smoke and heat from the carbons. The light was brilliant white and very much more intense than that obtained from either the low carbon arc or the Pointolite lamp, as shown by spectrographic analysis.

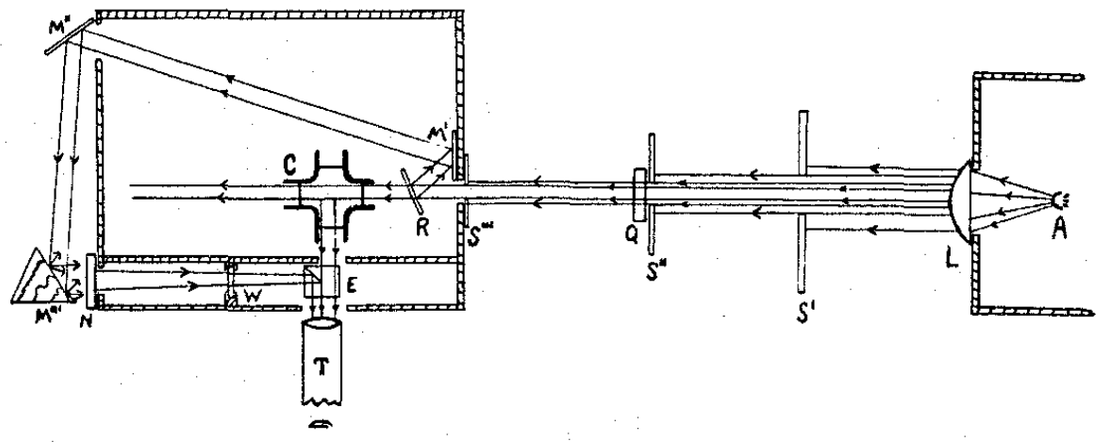


FIG. 3

L is a large focusing lens of about 8″ focal length used to make parallel the light from the arc. It was the only lens used in the entire apparatus.

S′, *S″*, *S‴* are three slits placed in the path of the incident beam in such a way as to cut down successively this beam, besides ridding it of all divergent rays from the lens L. The distance between two adjacent slits was approximately 2 ft.; S‴ was the smallest slit, being about 1/2″ square, giving a steady, uniform, parallel beam of light through the cross.

Q is a cell containing an aqueous solution of quinine sulphate (about 7%) which was used to remove the ultra-violet light (spectrographic analysis showed that this filter cuts off all wave-lengths shorter than 4078 Å) from the incident beam. This solution could be kept for some time (a month or more) without losing this property, although constant exposure to light turned it decidedly yellow after three weeks.

R is a plate of plane glass which deflects a small portion of the incident beam to be used as the comparison light. Since it was arranged just in front of the cross any change in the intensity of the incident light would not affect the ratio of the reflected and transmitted light. The small angle, 12°, at which this plate was set would produce only a negligible proportion of polarized light in the transmitted beam.

M′ M″ are plate glass mirrors arranged to transmit this comparison beam to the outside of the measuring-box. *M‴* is a paper reflector which diffuses

[1] J. Phys. Chem., **24**, 485 (1920).

this comparison light through the colour-filter N. Boundary lines were marked on M''' so that the illuminated patch on M''' could always be brought to the same position and area.

N is a solution of ammoniacal copper sulphate of such concentration that the colour of the comparison beam after passing through it was a perfect match to the blue of the scattering in the solution to be measured. The colour of this comparison blue could be regulated by changing the solution in the cell itself, and its intensity by the use of suitable thin paper filters behind the cell.

W is an optical wedge, arranged in a vertical position half way between the copper sulphate cell and a Lummer-Brodhun cube. A scale was attached to the upper end of the wedge, and the relation of this scale to scattering values was obtained from a "transmission" vs. "scale readings in cms." graph supplied for the wedge by the Eastman Kodak Company in November, 1923. These transmission values were checked by the author photometrically in January, 1926, and found to be unchanged. A compensating wedge to produce a uniform field was placed to the left of the wedge, and a suitable slit on the opposite side.

C is the cross containing the solution whose relative light scattering value was to be found. The blue scattering was observed through a third arm of the cross at right angles to the incident beam in the solution.

E is a Lummer-Brodhun cube which brings into juxtaposition the scattering blue from the cross and the comparison blue from the wedge. These two blues were observed by a telescope, T, which was focused directly on a narrow slit placed on the front face of the cube. They were matched by the proper adjustments of the optical wedge and readings were taken when a visual observation showed that these two blues had been matched in intensity.

It should be noted that suitable screens and hoods were always used to cut off all stray light. Further, readings were only taken after the eye had become accustomed to the darkness of the room, and the faintness of the blues to be matched. This was found to take ten minutes or more, depending on the observer, but it was always noted that once the eye had become accustomed to the faint colours good checks could be obtained. A set of readings, showing the position of the wedge in cms., taken at random from the author's notes (March 24, 1926), gives an idea of the accuracy obtainable from this arrangement. In this case an 11.04% potassium chloride solution was measured against the methyl alcohol comparison standard.

Methyl Alcohol 5.4; 5.8; 5.1; 5.2; 4.9; 4.9; 5.8; 5.5; 4.8; 5.6; 5.2; 4.9; 5.6. Average 5.28.

Potassium Chloride Solution 10.9; 11.3; 10.7; 11.1; 10.9; 11.2; 11.1; 11.1; 11.4; 10.6. Average 11.03.

The transmission values for these averages are:

Cms. readings	Trans. values
5.28	0.377
11.03	0.147

Therefore, scattering of the KCl sol. (alc. = 1) is

$$0.147/0.377 = .390.$$

The alcohol-benzene factor, found during this period, being 0.225, the scattering of the KCl sol. (Benzene = 1) is $0.390 \times 0.225 = .088$.

Subsequently at intervals of one day these readings were repeated and further values for the scattering of this solution obtained. The final value of the scattering for this solution, given in Table III, was obtained by averaging these various values as found above. In this case they were: 0.088, 0.092

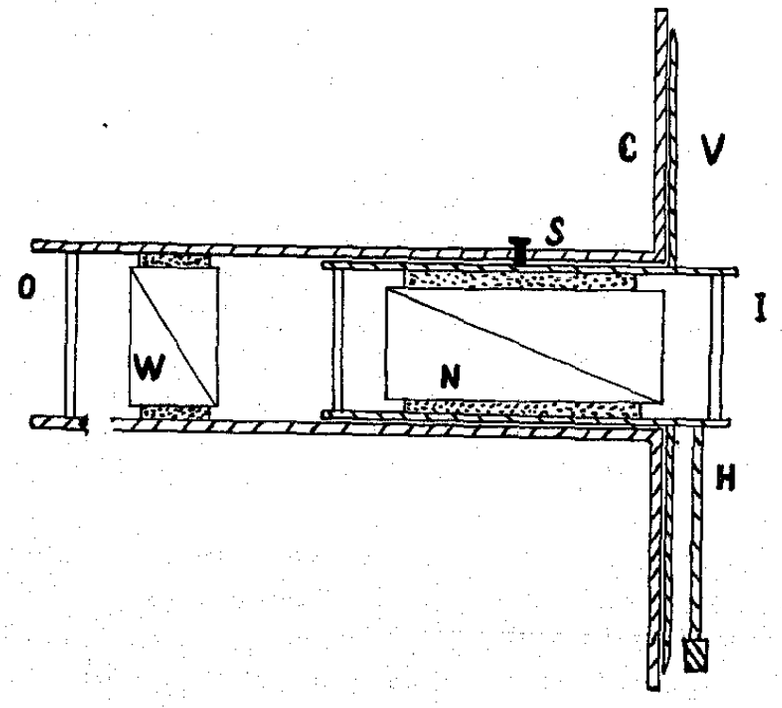


FIG. 4

and 0.088, giving a final average of 0.089. The absolute water-benzene factor being 0.069 (as found by the author) the final scattering value (water = 1) for this potassium chloride solution becomes $0.089/0.069 = 1.29$. All the scattering values given in subsequent tables were found by following this method.

Apparatus for measuring the depolarization factor (ρ) *of the scattered light.*

The apparatus used is essentially the same as that used by Martin[1] although the apparatus shown in Fig. 4, and to be described in some detail is a rigid instrument. The scattered light is observed through a double image Wollaston prism carefully orientated to give the vertically and horizontally polarized components of the scattered light. This (W) is set permanently in a brass sleeve to which is attached a circular scale (C). The resulting images are then equalized by rotating a Glan-Thompson prism (20 × 20 × 53 mm.), (N), which is set permanently in an inner sleeve (S), that can be rotated readily by means of the attached handle (H). A vernier (V) is at-

[1] J. Phys. Chem., **27**, 559 (1923).

tached to this inner sleeve and the readings of this vernier on the circular scale give the relative intensities of the two components. The $\tan^2\theta$ law is assumed.

As in the case of the light scattering measurements the results were obtained by averaging a set of 8 to 12 readings. The final values of ρ, tabulated later in this paper, were obtained by averaging a set of 3 to 4 averages obtained as above. A set of such averages obtained for the 11.04% potassium chloride solution, for which scattering data were given above, were 0.093; 0.097; 0.093; 0.095; giving a final average of 0.094, the value given in Table III.

These readings were all visual and were always taken for the same solution as used in the light scattering measurements.

Standards used for measurements.

The permanent standard used was a cross of benzene, prepared dust-free by the distillation method. The benzene used was Kahlbaum's thiophene-free which was recrystallized once. This was found not to change its intensity of scattering value for at least a year, for a cross prepared twelve months after that above gave the same scattering. This cross of benzene was also used as a comparison standard for those solutions whose scattering values were fairly high. A cross of methyl alcohol was used as a comparison standard for those solutions whose scattering values were small (less than 3 times H_2O). Every time a series of light scattering measurements was being made the benzene factor of the methyl alcohol standard was found by measurement, for it was noted that the intensity of the scattering of one of the alcohol standards had increased during two months by about 10%. The values for the freshly prepared dust-free methyl alcohol and water were found by measuring against the benzene. The methyl alcohol used was Kahlbaum's, fractionated in a special vertical still (fraction used at 66°C.). The values for these freshly prepared standards are given in Table I, where values obtained by other observers are also included. Results obtained by Rocard and Cabannes are also in close agreement.

TABLE I

	Light Scattering ($H_2O=1$)			Depolarization Factor (ρ)		
Liquid	Sweitzer	Martin	Krishnan	Sweitzer	Martin	Krishnan
Water	1.00	1.00	1.00	0.109	0.086*	0.096
Methyl alcohol	2.77	2.80	3.71	0.103	0.071	0.082
Benzene	14.5	14.7	15.0	0.480	0.485	0.470

* Martin now accepts value of 0.109 for water.

These results show the agreement of the values obtained by the present method of procedure with those given by Martin and Krishnan. The agreement between the author's and Martin's results for scattering is very good, while the author's value of ρ for water is near the value now accepted by most investigators (this is 0.110). Krishnan's high scattering for methyl alcohol was probably due to impurities.

Theoretical Considerations

The Einstein-Smoluchowski-Cabannes formula for salt solutions.

The generally accepted form of the Einstein formula for a two component solution is

$$I=\frac{EV\pi^2RT}{r^2{}_2N\lambda^4}\left[\frac{(\partial\epsilon/\partial k)^2}{m_1v_2\partial p_2/\partial k}+\frac{\beta(\mu^2-1)^2(\mu^2+2)^2}{9}\right]\frac{6(1+\rho)}{6-7\rho} \quad (1)$$

where the factor $6(1+\rho)/(6-7\rho,)$ due to Cabannes[1] is called the Cabannes correction factor. ρ, the depolarization factor, is defined as the ratio of the intensity of the weak to that of the strong polarized component of the scattered light, the incident light being unpolarized. The other symbols have the significance given by Raman[2].

In order to calculate the relative values of the light scattering ($H_2O=1$) for the solutions studied[3] it is only necessary to take account of the terms after the constant factor before the bracket,

$$K=\frac{EV\pi^2RT}{r^2{}_2N\lambda^4}$$

Expressing composition as x (grams salt per 100 g. solution) and the pressure and compressibility in more convenient units (1) becomes

$$I=K\left[\frac{\left(-\frac{\partial\mu^2}{\partial x}\cdot\frac{x^2}{100}\right)^2}{m_1v_2\left(-\frac{13.6\times981}{10}\cdot\frac{\partial p_{mm}}{\partial x}\cdot\frac{x^2}{100}\right)}+\frac{\beta_a(\mu^2-1)^2(\mu^2+2)^2}{9\times981\times76\times13.6}\right]\frac{6(1+\rho)}{6-7\rho} \quad (2)$$

where the values for $\partial\mu^2/\partial x$ and $\partial p_{mm}/\partial x$ are read directly from graphs in which μ^2 and vapour pressure respectively have been plotted against x, p_{mm} is vapour pressure in mm. of mercury and β_a is compressibility per atmosphere.

The Cabannes Factor.

The Cabannes correction factor was only intended to correct for the observed imperfection in the polarization of the scattered light in gases, where the ρ's are relatively small. Since then, however, it has been applied to the case of liquids where the ρ's as a rule are much greater. That this use of the Cabannes factor is not entirely satisfactory is suggested by the results of Krishnan[4] where the deviation of the observed and calculated values increases in general with increasing ρ (the calculated values becoming rapidly greater). This deviation, however, is not apparent in the results in this report for salt solutions with a high value of ρ (about 0.4).

Ramanathan[5] has derived a formula for the light scattering in liquids. Trial of this formula, using a number of liquids with ρ's varying from 0.12

[1] Ann. Phys., **15**, 5 (1921).

[2] Phil. Mag., **45**, 220 (1923).

[3] In using the above formula for salt solutions, possible fluctuations of the ratio of concentration of anion and cation and of the equilibrium $NaCl \leftrightarrows Na+Cl$ are ignored.

[4] Phil. Mag., **50**, 697 (1925).

[5] Proc. Indian Assoc., **8**, Part III (1923).

to 0.78, showed that the agreement between the observed and calculated results was not as good as that obtained by the use of formula (1) in this paper. In view of the increasing amount of experimental data in the literature on this subject, it is hoped that someone will succeed in deriving a formula for liquids more in accord with the facts.

Concentration, Density and Orientation Scattering.

In relation (2), I, the intensity of the scattered light, can be considered to be the sum of three terms; the two terms inside the brackets ($\times$K) and a third term which can be calculated from the Cabannes factor. The first term inside the brackets ($\times$K) may be called the composition scattering,[1] C_a, and the second term inside the brackets ($\times$K), the density scattering, D_a.

The Cabannes factor increases the value of $(C_a+D_a)K$ by the amount of scattering attributed to molecular anisotropy. Consequently, the third term called orientation scattering, O_a is given by

$$O_a = K\left[\left(C_a + D_a\right) \left(\frac{6(1+\rho)}{6-7\rho} - 1\right) \right] \qquad (4)$$

These divisions are arbitrary, but in subsequent tables are listed for each case together with the total calculated scattering, all relative to total scattering for water = 1. The relative importance of the data involved in these three effects may be gauged for each solution by inspection of the calculated results in the tables as well as from the graphs.

Results—Observed and Calculated

Symbols. The meaning of the symbols used in the subsequent tables is:

% grams anhydrous salt in 100 g. of solution. (In the recipes throughout this paper, % for the reagent solutions used in the formation of the precipitates means grams per 100 cc. of solution.)
This was determined by analysis after measurements had been concluded. Analysis was made by using a pyknometer and specific gravity tables by the author indicated.

S.G.^{t} Specific gravity as determined above by the pyknometer at the temperature given.

M Number of formula weights of salt per litre of solution.

μ^t Refractive index interpolated graphically from values by the author indicated.

β^t Isothermal compressibility per atmosphere interpolated graphically from results by the author indicated. The temperature and pressure used by each author are given.

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[1] The subscript *a* distinguishes these absolute values from the relative values used subsequently in the tables and graphs. From Martin's measurement of the absolute scattering of ether (J. Phys. Chem., **26**, 75 (1922)) and his ether-water ratio the absolute scattering for water is 1.77×10^{-6} for $\mu = 4358 \times 10^{-8}$ cm., while formula (2) gives 2.968×10^{-6}. The fair agreement between the calculated and observed relative scattering for salt solutions shown in this paper suggests, therefore, that a factor—about 0.6—should be applied to formula (2) in order to bring it into better agreement with the observed scattering of salt solutions.

p^t_{mm} Vapour pressure of the solution at the temperature given; this pressure in the case of the acids is the partial pressure of the aqueous vapour. It has been assumed that the value $\Delta p/p$ at 20°C. is given sufficiently accurately by the corresponding value at 100°C.

ρ Depolarization factor defined previously and measured by the author. ρ_1 is the depolarization factor found when the quinine sulphate was removed from the path of the incident beam and therefore refers to the light consisting of the sum of the true scattering and the fluorescence present in certain solutions. The purpose of this measurement is explained under section "Fluorescence".

O.S. Total observed relative scattering ($H_2O = 1$).

O_1 Relative orientation scattering "observed value" calculated from the relation $O_1 = I - I/C.F.$, where I = O.S. and C.F. = Cabannes factor.

C.S. Total calculated relative scattering ($H_2O = 1$) obtained by the use of Equation 2.

C. Composition part of the total calculated relative scattering (C.S.).

D. Density part of the total calculated relative scattering (C.S.)

O. Orientation part of the total calculated relative scattering (C.S.).

The values of ρ for all solutions are plotted in Graphs 1 and 2. The values of O.S., C.S., C., D., and O. are plotted in Graphs 3 to 17 inclusive, (one graph for each set of solutions).

The Graphs.

In plotting the graphs for the observed values a smooth curve was drawn to include values for the 0% and the higher percent solutions. This was done because water has been measured many times by different observers and because, when duplicate solutions were prepared and measured, the best agreement was found for the higher concentrations.

The plotting of the graphs for the calculated values was necessarily somewhat arbitrary, for, whereas the observed values of ρ used in the calculations are probably more reliable for the higher concentrations, the values for $\partial p_2/\partial k$ are not necessarily so.

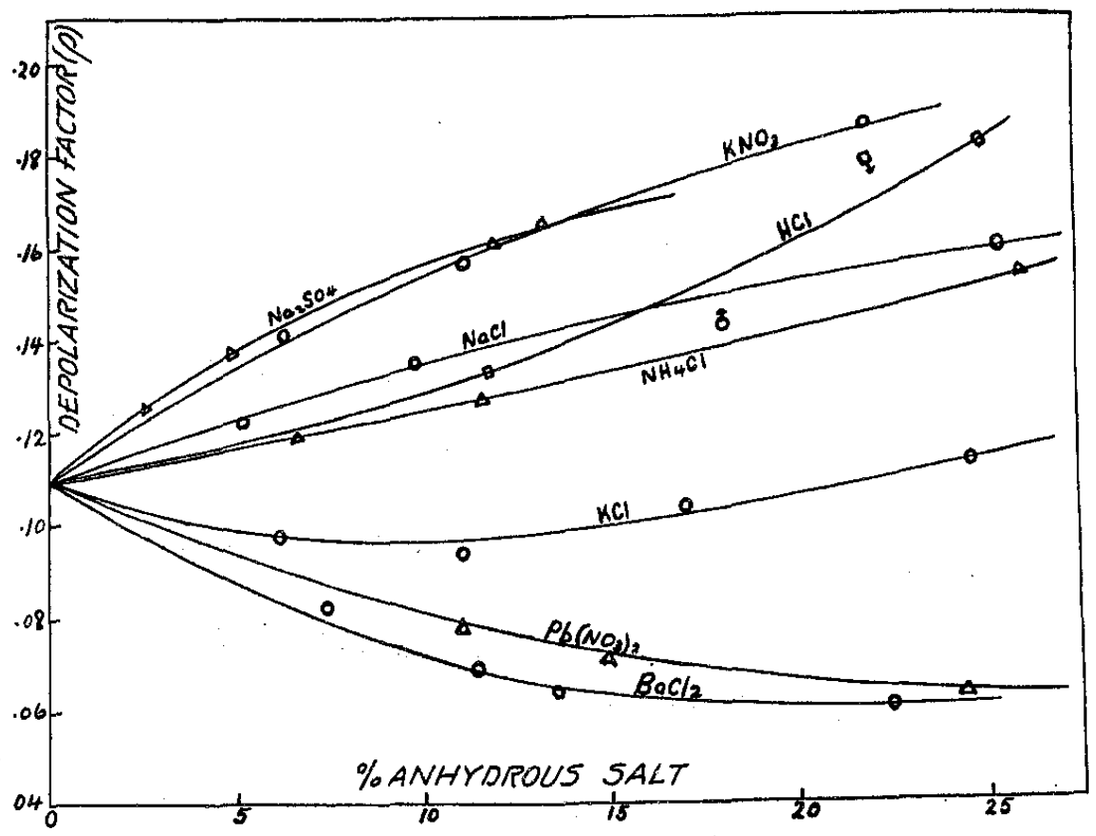
Sodium Chloride.

The recipe given is that used in the preparation of the 9.80% sodium chloride solution in Table II, and is a general recipe for all sodium chloride solutions.

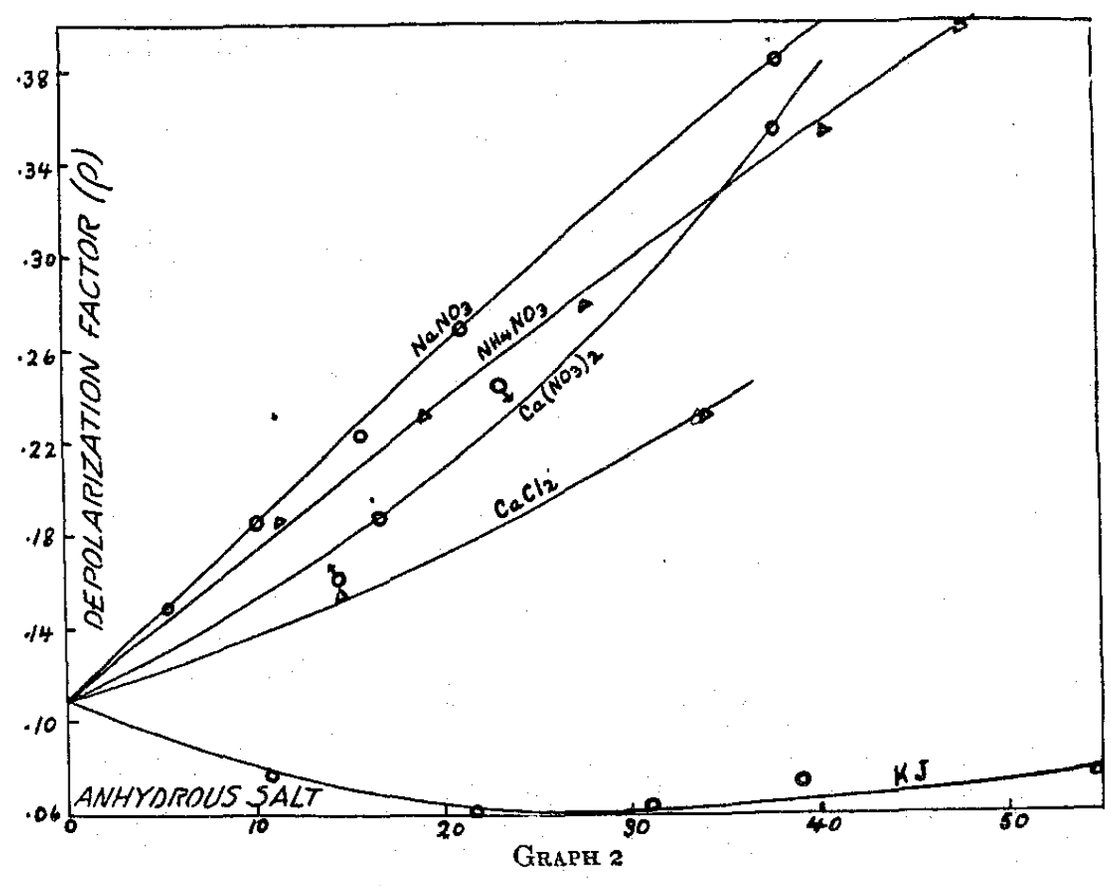
To a 2 litre flask were added in order—

1875 cc. of app. 10% sodium chloride (de Haen) solution.
10 cc. of chlorine water, containing 0.04 g. chlorine,
57 cc. of app. 15% sodium hydroxide (Baker's) solution,
69 cc. of app. 12% aluminium chloride (Baker's C.P.) solution,

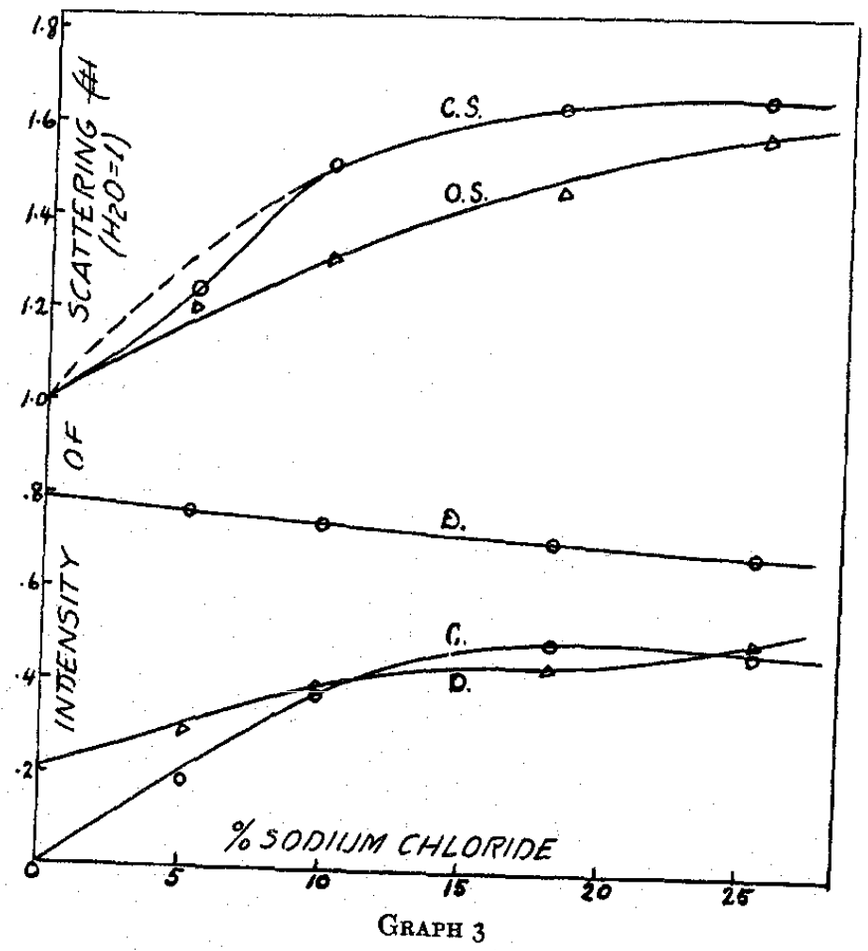
where the last two quantities were determined by titrating in the presence of 10% sodium chloride solution, using phenolphthalein as indicator.



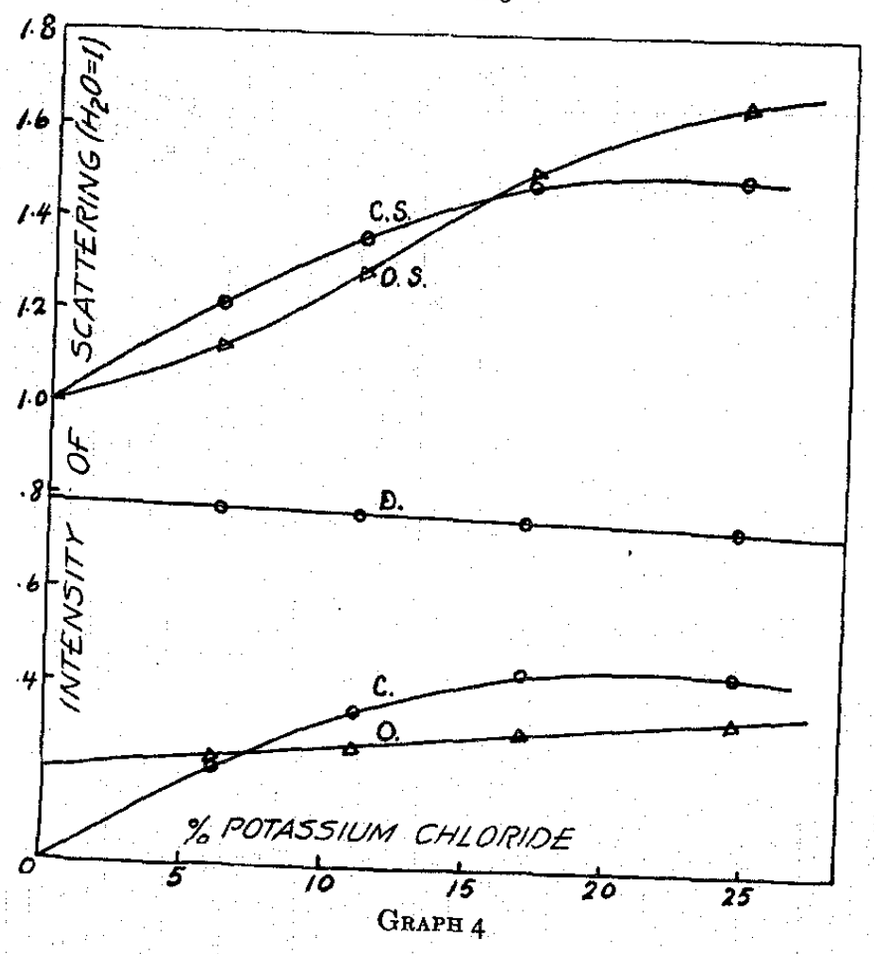
GRAPH 1



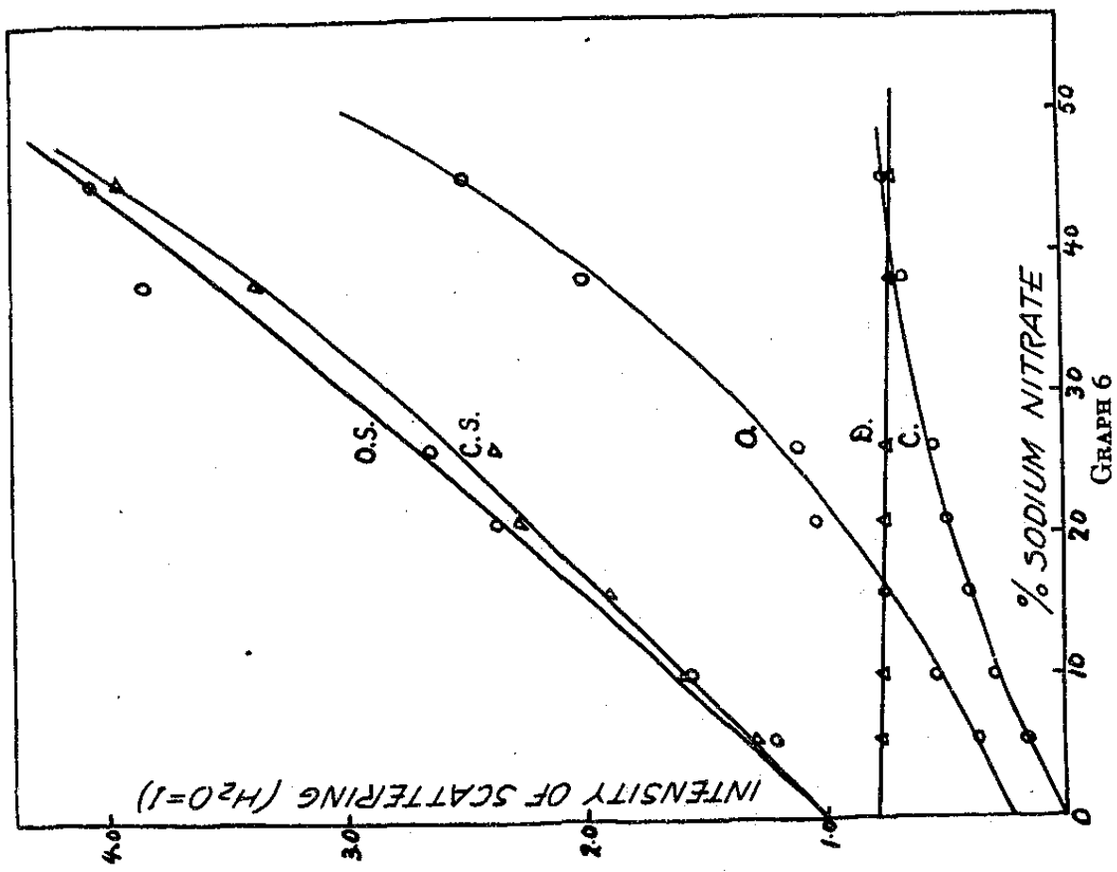
GRAPH 2



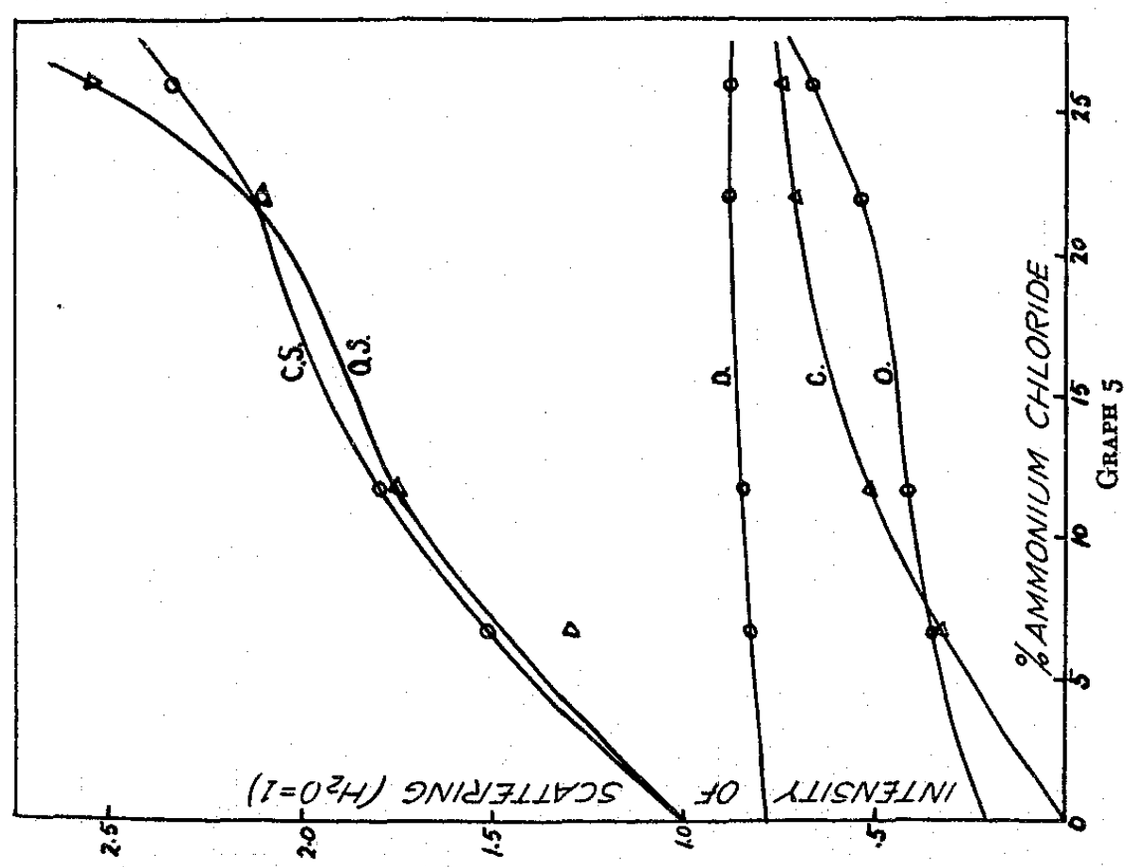
GRAPH 3



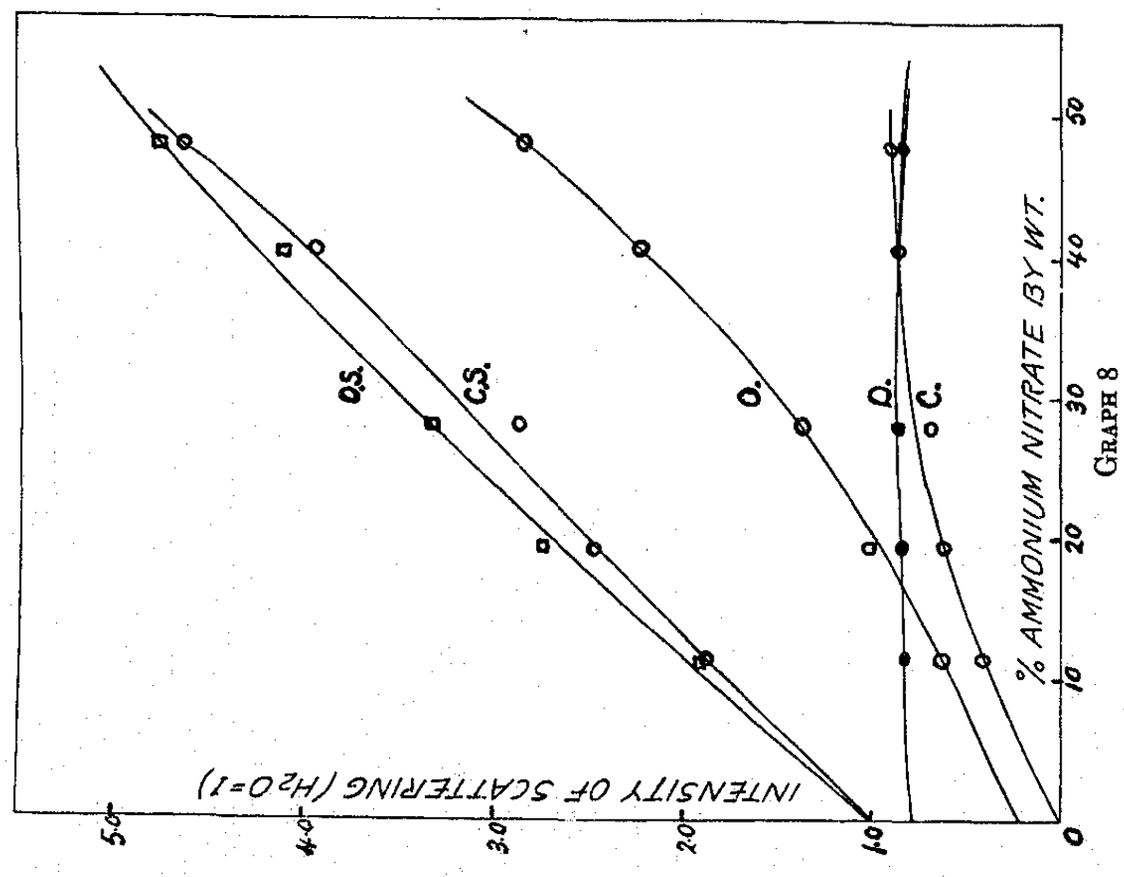
GRAPH 4



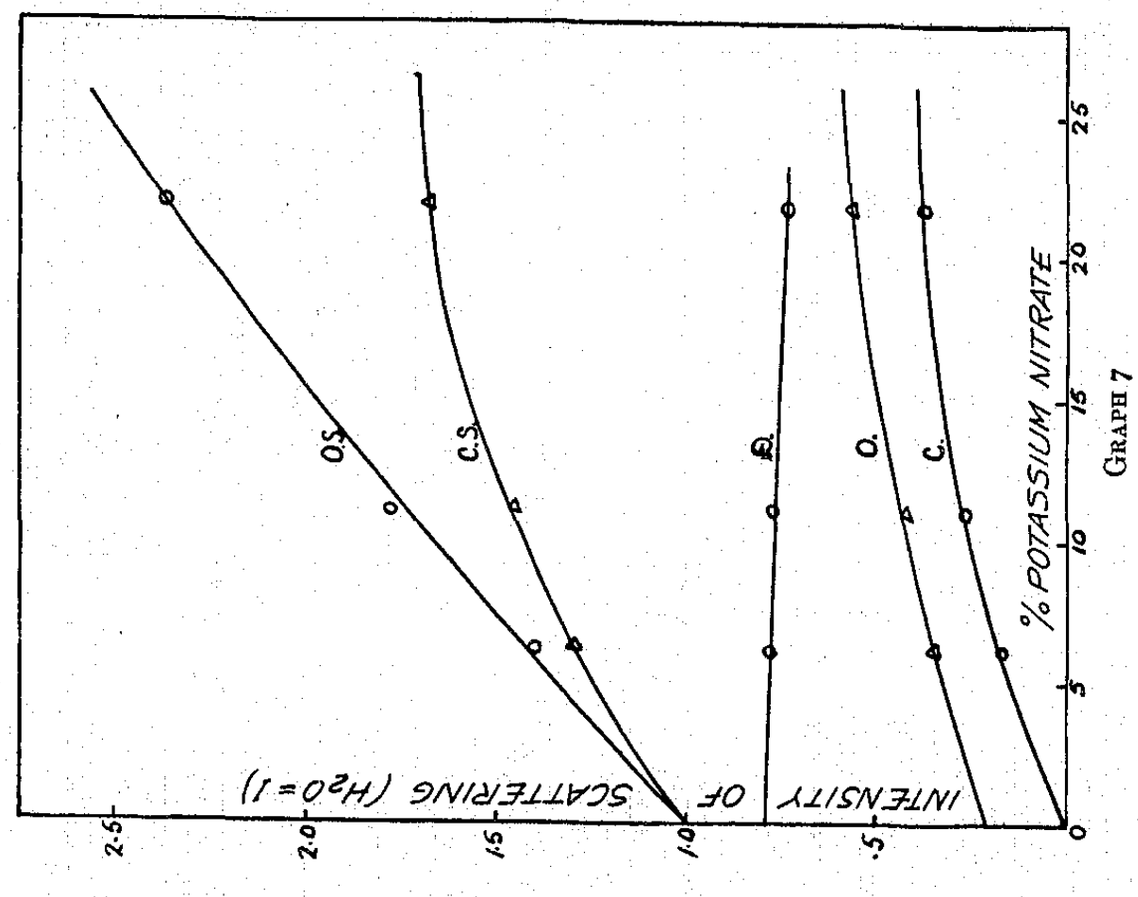
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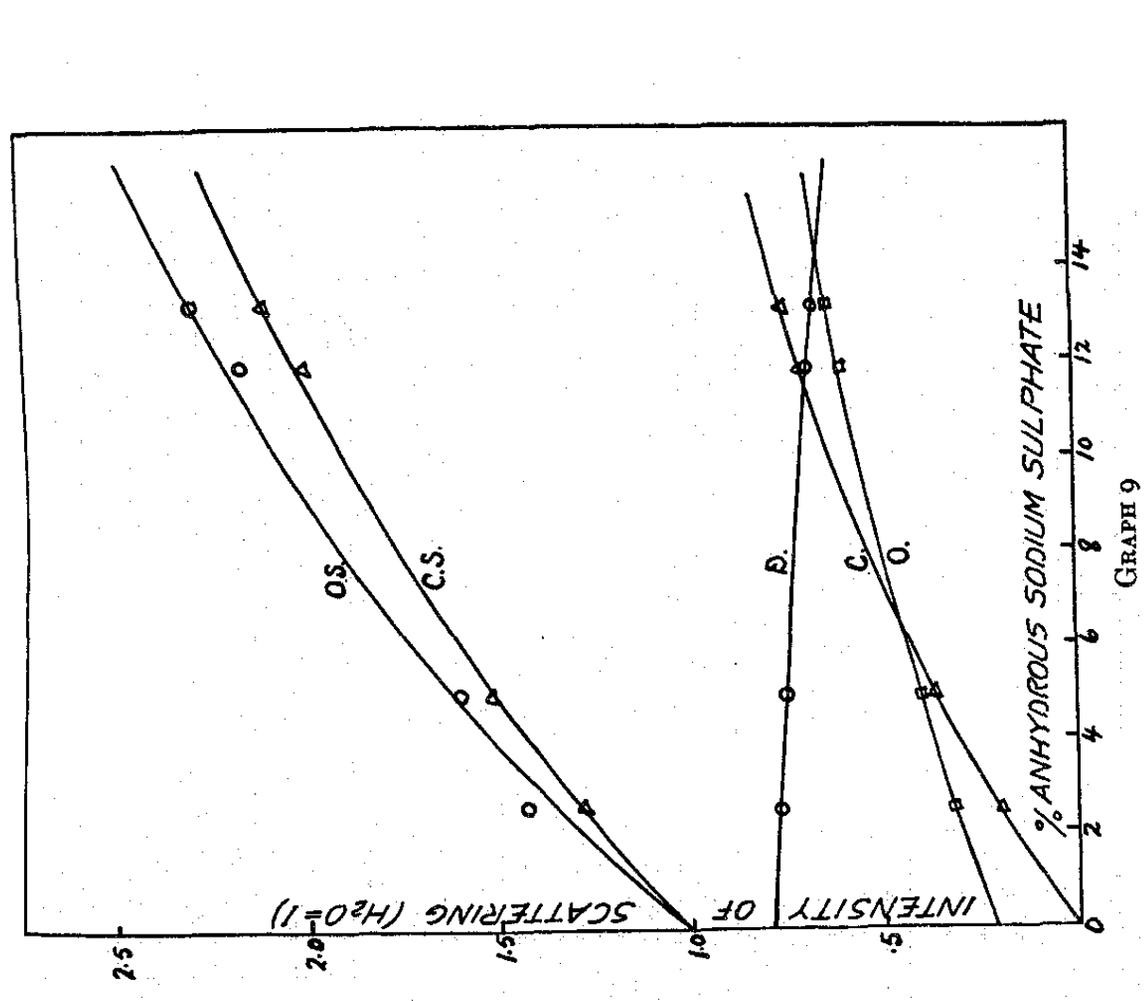
GRAPH 5



GRAPH 8

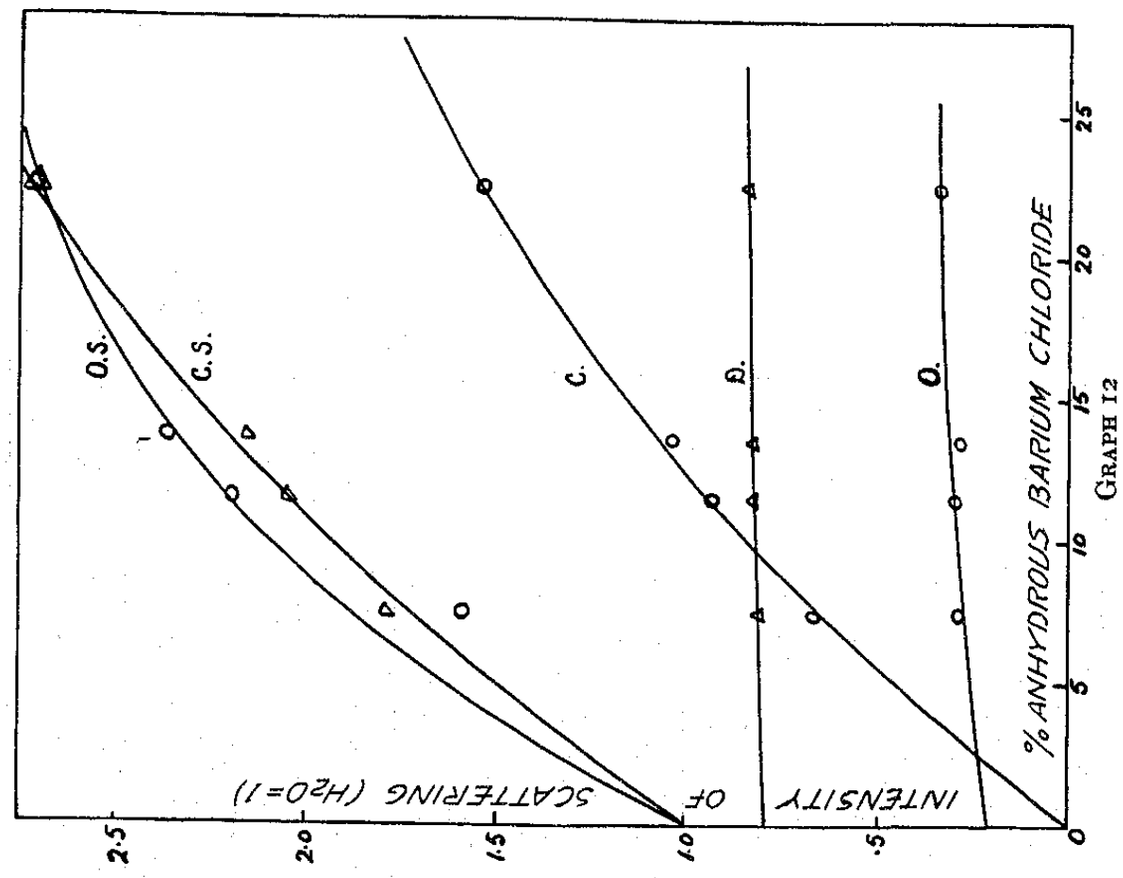


GRAPH 7

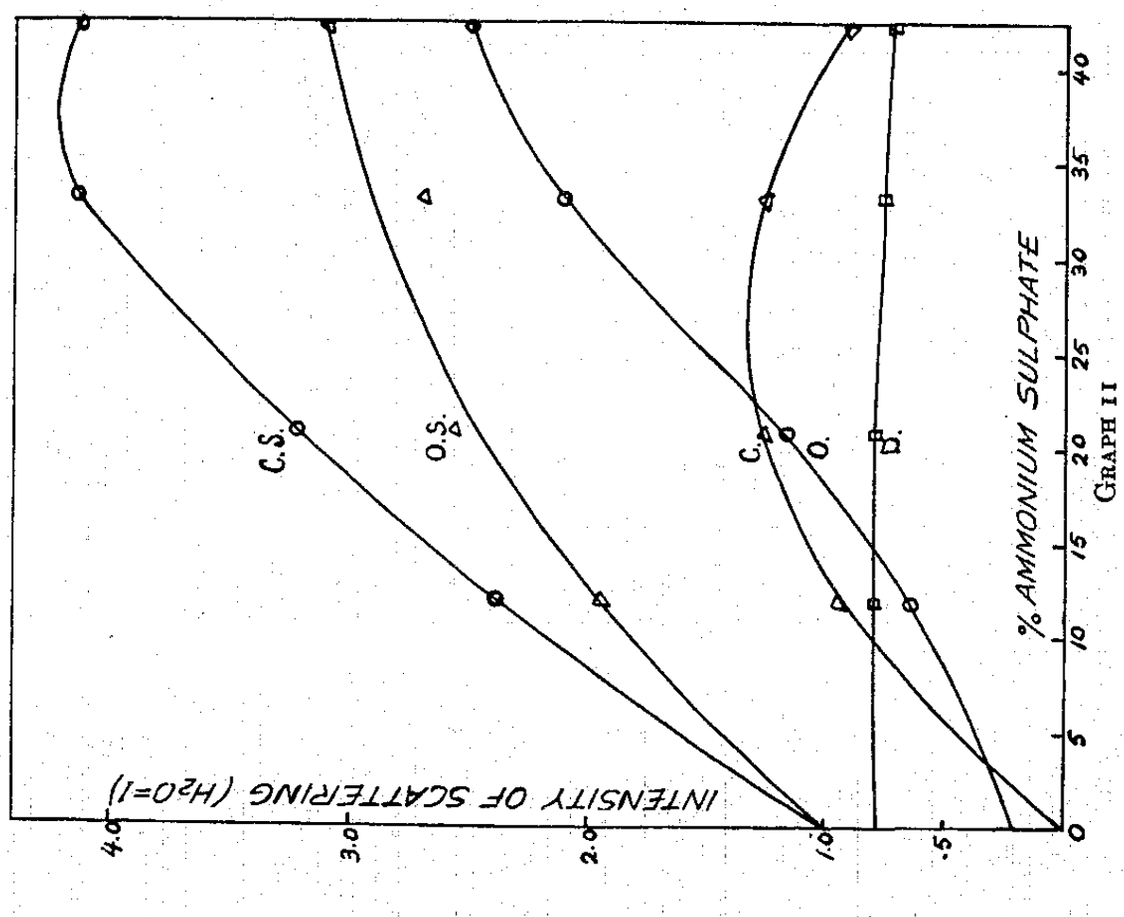


GRAPH 10

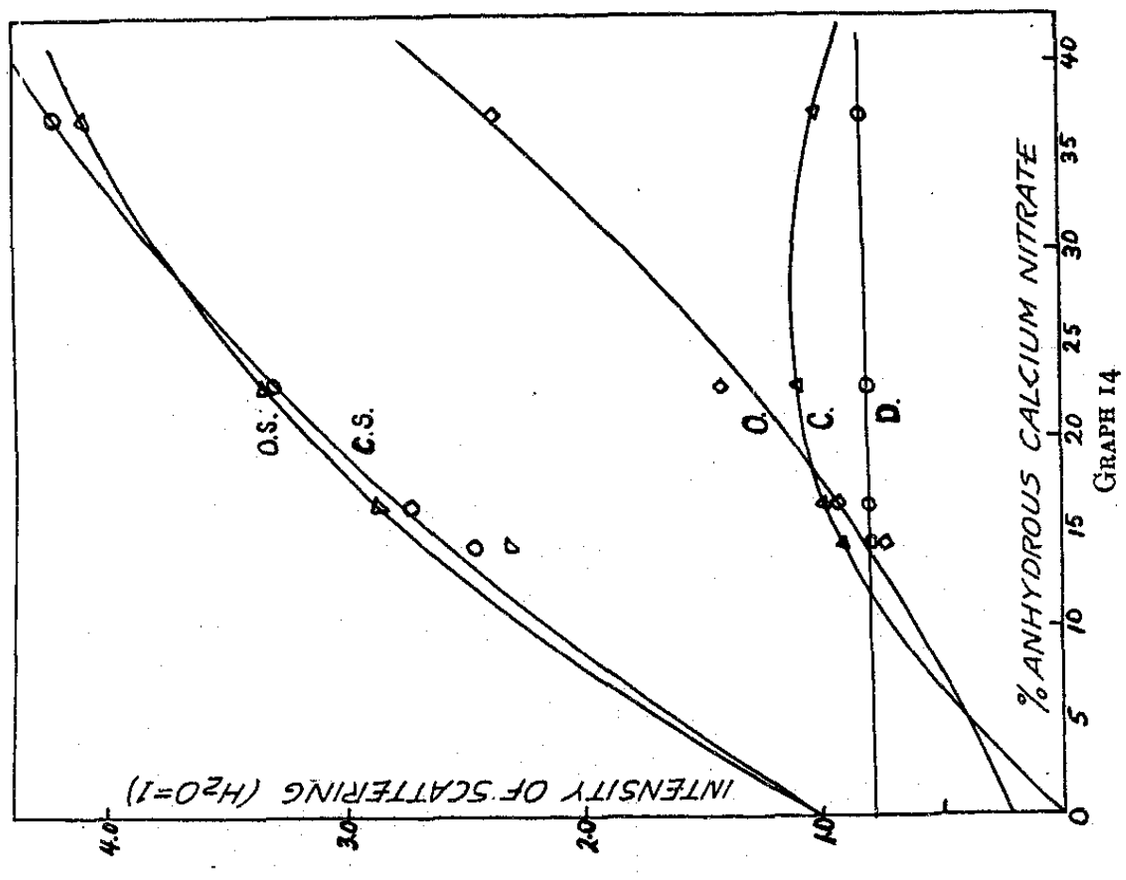
GRAPH 9



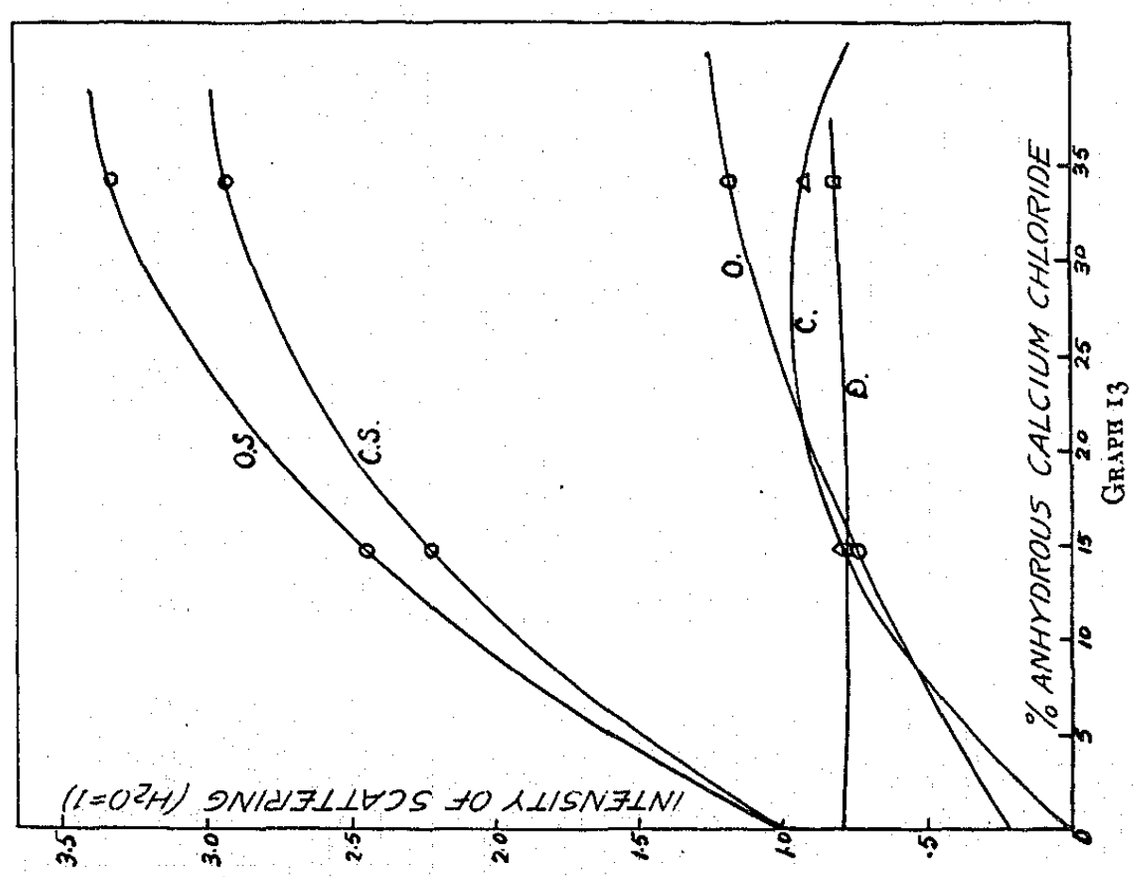
GRAPH 12



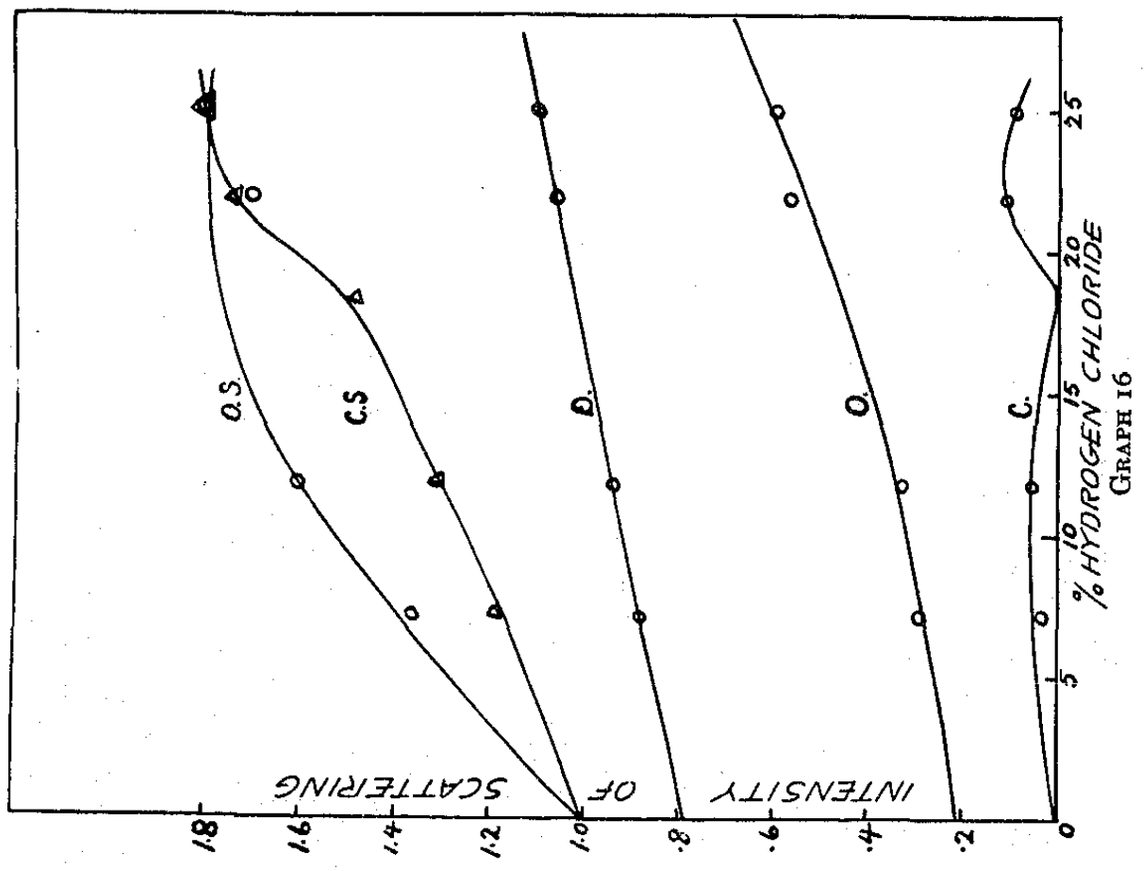
GRAPH 11



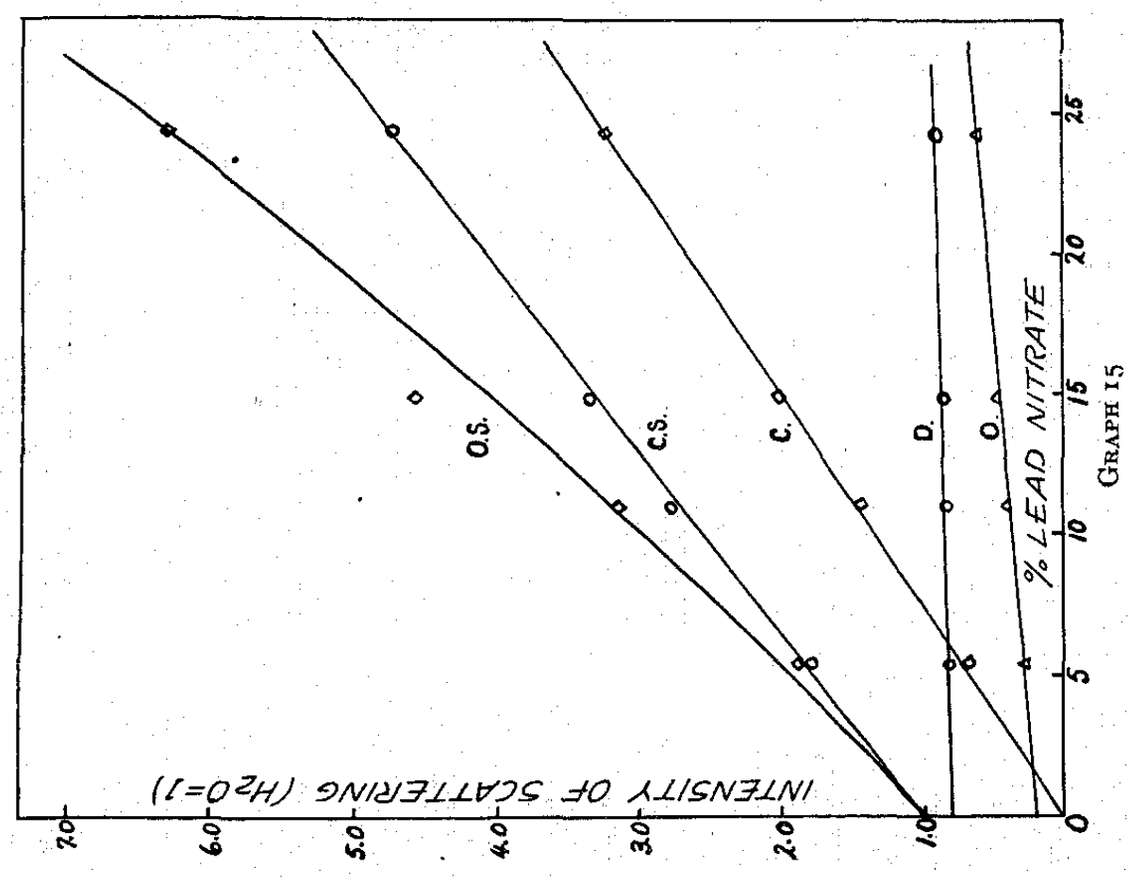
GRAPH 14



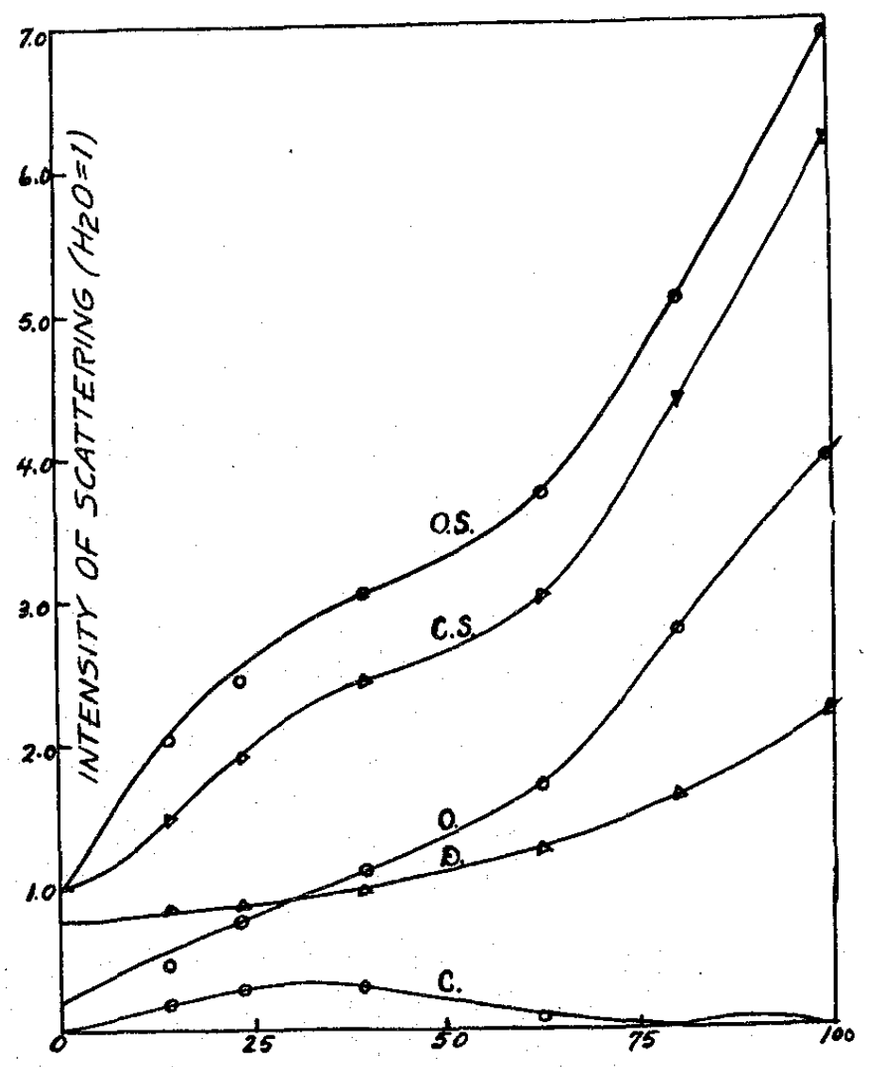
GRAPH 13



GRAPH 16



GRAPH 15



GRAPH 17

TABLE II

Sodium Chloride

%	S.G. $20/20^\circ$ Ka.	M	$\mu_D^{18^\circ}$ Di.	$\beta^{20^\circ} \times 10^6$ 1-300 at. Gi.	$p^{mm}_{100^\circ}$ Ta.	ρ	ρ_1
0	1.000	0	1.3332	44.37	760.0	0.109	0.125
5.12	1.035	0.91	.3420	39.90	736.7	.122	.165
9.80	1.069	1.79	.3503	36.30	712.8	.135	——
18.06	1.132	3.49	.3651	31.00	656.0	.143	——
25.36*	1.191	5.16	.3791	27.10	591.0	.160	.216

* Duplicate solution gave O. S. = 1.60 and ρ = .160.

Ka.—Karsten: "Landolt-Börnstein Tables", 392 (1923).

Di.—Dinkhauser: "L. B. Tables", 992 (1923).

Gi.—Gilbault: Z. physik. Chem., **24**, 385 (1897).

Ta.—Tammann: Wied. Ann., **24**, 530 (1885).

TABLE II continued

$\frac{6(1+\rho)}{6-7\rho}$	Observed Scattering ($H_2O=1$) Total C. S.	Orient. O_1	Calculated Scattering ($H_2O=1$) Total C. S.	Comp. C.	Dens. D.	Orient. O.
1.271	1.00	0.21	1.00	0	0.79	0.21
1.308	1.20	.28	1.24	.184	.76	.29
1.348	1.31	.34	1.51	.378	.74	.39
1.366	1.46	.39	1.64	.491	.71	.44
1.427	1.58	.47	1.66	.474	.69	.50

Results in Table II and Graphs 1 and 3 show for the sodium chloride solutions:—Values of ρ slightly larger than ρ for water; fair agreement between the calculated and observed values for the relative intensity of the light scattering; a relatively high density scattering and a maximum for the composition scattering.

Potassium Chloride.

Recipe for the 24.60% solution given in Table III:—
To 1100 cc. flask were added in order—

1050 cc. of about 25% potassium chloride (Merck's C.P.) solution,
2 cc. of chlorine water, containing 0.01 g. chlorine,
25 cc. of about 20% potassium hydroxide (Merck's) solution,
21 cc. of about 13% aluminium chloride (Baker's C.P.) solution,

where these last two quantities were obtained by titrating in the presence of 25% potassium chloride solution using phenolphthalein as indicator.

TABLE III
Potassium Chloride

%	S. G. $15/15^\circ$ Ge.	M	$\mu_D^{17.5^\circ}$ Wa.	$\beta^{20^\circ} \times 10^5$ 1-300 at. Gi.	$p_{100^\circ}^{mm}$ Ta.	ρ	ρ_1
0	1.000	0	1.3332	44.37	760.0	.109	.125
6.12	1.040	.85	.3415	40.80	739.2	.097	.135
11.04	1.073	1.59	.3482	38.20	720.0	.094	.154
17.00	1.114	2.54	.3567	35.23	693.0	.104	.207
24.60	1.170	3.86	.3675	31.80	648.8	.113	.195

$\frac{6(1+\rho)}{6-7\rho}$	Observed Scattering ($H_2O=1$) Total O. S.	Orient. O_1	Calculated Scattering ($H_2O=1$) Total C. S.	Comp. C.	Dens. D.	Orient O.
1.271	1.00	.21	1.00	0	0.79	0.21
1.237	1.12	.22	1.22	.215	.77	.23
1.228	1.29	.24	1.36	.339	.76	.26
1.257	1.51	.31	1.48	.424	.75	.30
1.282	1.65	.36	1.50	.429	.74	.33

Ge.—Gerlach: "Chemists Handbook", 298 (1919).
Wa.—Wagner: "L. B. Tables", 988 (1923).
Gi. and Ta.—See references under Table II.

Results in Table III and Graphs 1 and 4 show for the potassium chloride solutions: values of ρ for small concentrations lower than that for water and having a minimum value; fair agreement between the observed and calculated relative scattering, and results of the same order as found for the sodium chloride solutions, in the case of the arbitrary divisions.

Ammonium Chloride.

The standard recipe for these solutions is given under section "Dust-free Salt solutions" (p. 4000). It is general for all ammonium chloride solutions.

TABLE IV
Ammonium Chloride

%	S. G. 15/15° Ge.	M	$\mu_D^{17.5°}$ Wa.	$\beta^{15°} \times 10^6$ 1-10 at. Sch.	$p_{100°}^{mm.}$ Ta.	ρ	ρ_1
0	1.000	0	1.3332	46.40	760.0	.109	.125
6.67	1.019	1.27	.3460	43.80	728.0	.119	.229
11.67	1.034	2.25	.3555	41.50	701.1	.127	.280
22.00*	1.063	4.37	.3753	36.23	638.0	.132	.244
26.00	1.074	5.22	.3829	34.00	611.0	.154	.327

	Observed Scattering ($H_2O = 1$)		Calculated Scattering ($H_2O = 1$)			
$\frac{6(1+\rho)}{6-7\rho}$	Total O. S.	Orient. O_1	Total C. S.	Comp. C.	Dens. D.	Orient. O.
1.271	1.00	.21	1.00	0	.79	.21
1.300	1.29	.30	1.51	.336	.82	.35
1.323	1.76	.43	1.79	.512	.84	.44
1.339	2.12	.54	2.12	.703	.88	.54
1.406	2.55	.74	2.33	.782	.87	.67

* Duplicate sol. gave: S. G. 1.062, % 21.60, ρ .132, O. S. 2.11

Ge.—Gerlach: "L. B. Tables", 390 (1923).
Wa.—Wagner: "L. B. Tables", 989 (1923).
Sch.—Schumann: Wied. Ann., **31**, 14 (1887).
Ta.—Tammann: Reference under Table II.

Results in Table IV and Graphs 1 and 5, show for these solutions: Values of ρ of the same order as those for the sodium chloride solutions; fair agreement between the observed and calculated relative scattering, and a larger observed scattering than that for the previous chlorides of the same concentration.

Sodium Nitrate.

Recipe for the 45.25% solution given in Table V:

To a 2 litre flask were added in order—

1906 cc. of about 46% sodium nitrate (Baker's C.P.) solution,
5 cc. of chlorine water, containing 0.02 g. chlorine,
48 cc. of about 28% aluminium nitrate (Merck's C.P.) solution,
46 cc. of about 15% sodium hydroxide (Merck's) solution,

where these last two quantities were obtained by titrating in presence of 45% sodium nitrate solution, using phenolphthalein as indicator.

TABLE V
Sodium Nitrate

%	S. G. 20/20° Ba.	M	$\mu_D^{25°}$ Sw.	$\beta_{.10^6}^{20°}$ 1-300 at. Gi.	$p_{100°}^{mm.}$ Ta.	ρ	ρ_1
0	1.000	0	1.3325	44.37	760.0	.109	.125
5.50	1.036	.67	.3388	41.62	744.5	.148	.197
10.20	1.070	1.28	.3444	39.40	728.8	.185	.226
15.90	1.112	2.08	.3512	36.90	708.6	.222	.299
21.10	1.153	2.86	.3576	34.70	687.5	.268	.266
26.25	1.195	3.69	.3637	32.65	665.5	.270	.381
38.10	1.300	5.83	.3787	28.25	606.5	.375	.384
45.25	1.371	7.30	.3887	25.80	565.9	.413	.413

	Observed Scattering ($H_2O=1$)		Calculated Scattering ($H_2O=1$)			
$\frac{6(1+\rho)}{6-7\rho}$	Total O. S.	Orient. O_1	Total C. S.	Comp. C.	Dens. D.	Orient. O.
1.271	1.00	0.21	1.00	0	.79	0.21
1.388	1.20	.33	1.30	.160	.77	.36
1.511	1.56	.53	1.59	.283	.77	.54
1.649	2.00	.79	1.90	.395	.76	.75
1.845	2.37	1.09	2.27	.483	.75	1.04
1.855	2.65	1.22	2.38	.542	.74	1.10
2.445	3.85	2.28	3.38	.662	.72	2.00
2.728	4.06	2.57	3.95	.734	.71	2.49

Ba.—Barnes: "L. B. Tables", 408 (1923).
Sw.—Sweitzer: See Table XX in this report.
Gi.—Gilbault: See reference under Table II.
Ta.—Tammann: See reference under Table II.

Results in Table V and Graphs 2 and 6 show for these solutions: Values of ρ that increase rapidly with concentration; good agreement between the observed and calculated relative scattering; an orientation scattering which for the higher concentrations forms the major part of the total scattering and which increases rapidly with concentration, due to high values of ρ.

Potassium Nitrate.

Recipe for the 21.80% solution given in Table VI:
To a 2 litre flask were added in order—
1890 cc. of app. 22% potassium nitrate (Merck's C.P.) solution,
5 cc. of app. 5% mercuric chloride solution,
55 cc. of app. 20% potassium hydroxide (N.D. sticks) solution,
49 cc. of app. 28% aluminium nitrate (Merck's C.P.) solution,
where these last two quantities were determined by titrating in the presence of 22% potassium nitrate solution, using phenolphthalein as indicator. The mercuric chloride was used as a disinfectant, having germicidal properties when present in the ratio of 1 part in 10,000. Quantitative tests showed, as in the case of chlorine, that this addition had no measurable effect on the scattering.

TABLE VI
Potassium Nitrate

%	S. G. $15°$ Chv.	M	$\mu_D^{17.5°}$ Wa.	$\beta_{.10^6}^{20°C.}$ 1-40 at. Sw.	$p_{mm.}^{100°}$ Ta.	ρ	ρ_1
0	1.000	0	1.3332	45.80	760.0	.109	.125
6.25	1.040	.64	.3392	43.25	747.0	.141	.162
11.10	1.073	1.18	.3438	41.05	736.0	.156	.214
21.80	1.148	2.48	.3540	35.90	706.5	.187	.208

$\frac{6(1+\rho)}{6-7\rho}$	Observed Scattering ($H_2O=1$) Total O. S.	Orient. O_1	Calculated Scattering ($H_2O=1$) Total C. S.	Comp. C.	Dens. D.	Orient. O.
1.271	1.00	.21	1.00	0	.79	.21
1.366	1.40	.37	1.30	.172	.78	.35
1.414	1.78	.52	1.46	.267	.77	.42
1.518	2.37	.81	1.68	.376	.73	.57

Chv.—Chéneveau: "L. B. Tables", 406 (1923).
Wa.—Wagner: "L. B. Tables", 989 (1923).
Sw.—Sweitzer: See Table XX in this paper.
Ta.—Tammann: See reference under Table II.

Results in Table VI and Graphs 1 and 7 show: Values of ρ of about the same order as for the sodium nitrate solution of equal concentration; observed values for relative light scattering considerably larger than the calculated values.

Ammonium Nitrate.

Recipe for the 47.80% solution, given in Table VII:
To a 1100 cc. flask were added in order—

1050 cc. of app. 48% ammonium nitrate (Kahlbaum's) solution,
5 cc. of app. 5% mercuric chloride solution,
15 cc. of app. 28% ammonia (B. & A. C.P.),
36 cc. of app. 28% aluminium nitrate (Merck's C.P.) solution,

where these last two quantities were obtained by titrating in the presence of 48% ammonium nitrate solution, using indicators and precipitation method described under section "Dust-free Salt Solutions".

TABLE VII
Ammonium Nitrate

%	S. G. $17.5°$ Ge.	M	$\mu_D^{25°}$ Sw.	$\beta_{.10^6}^{20°}$ 1-40at. Sw.	$p_{100°}^{mm.}$ Ta.	ρ	ρ_1
0	1.000	0	1.3325	45.80	760.0	.109	.125
11.50	1.047	1.50	.3472	42.21	725.0	.187	.271
19.10	1.080	2.58	.3574	39.76	697.8	.231	.376
28.00	1.120	3.92	.3695	36.90	658.6	.278	.405
40.55	1.180	5.98	.3871	32.45	599.0	.353	.468
47.80	1.217	7.27	.3978	29.80	560.5	.398	.490

TABLE VII continued

$\frac{6(1+\rho)}{6-7\rho}$	Observed Scattering ($H_2O=1$) Total O. S.	Orient. O_1	Calculated Scattering ($H_2O=1$) Total C. S.	Comp. C.	Dens. D.	Orient. O.
1.271	1.00	.21	1.00	0	.79	.21
1.518	1.90	.65	1.87	.412	.82	.64
1.686	2.71	1.10	2.45	.620	.83	1.00
1.891	3.32	1.56	2.86	.659	.85	1.35
2.300	4.10	2.32	3.93	.855	.86	2.22
2.611	4.75	2.93	4.60	.909	.85	2.84

Ge. Gerlach: "L. B. Tables", 390 (1923).
Sw.—See Table XX in this report.
Ta.—Tammann: See reference under Table II.

Results in Table VII and Graphs 2 and 8 show: Large values of ρ, of the same order as in the case of the sodium nitrate solution of equal concentration; very good agreement between the observed and calculated relative scattering.

Sodium Sulphate.

Recipe for the 13.20% solution in Table VIII:
To a 2 litre flask were added in order—

1900 cc. of app. 14% sodium sulphate (Merck's) solution,
10 cc. of chlorine water, containing 0.04 g. chlorine,
47 cc. of app. 15% sodium hydroxide (Merck's) solution,
56 cc. of app. 32% aluminium sulphate (Merck's) solution,

where these last two quantities were obtained by titrating in the presence of app. 14% sodium sulphate solution, using phenolphthalein as indicator.

TABLE VIII
Sodium Sulphate

%	S. G. $17.5°$ Ba.	M	$\mu_D^{18°}$ Di.	$\beta_{.10^6}^{20°}$ 1-40 at. Sw.	$p_{100°}^{mm.}$ Ta.	ρ	ρ_1
0	1.000	0	1.3334	45.80	760.0	.109	.125
2.55	1.022	.183	.3372	43.60	755.4	.125	——
4.90	1.044	.360	.3407	41.50	750.6	.137	——
11.90	1.111	.931	.3510	35.70	736.0	.160	.246
13.20	1.124	1.05	.3530	34.70	733.0	.165	.330

$\frac{6(1+\rho)}{6-7\rho}$	Observed Scattering ($H_2O=1$) Total O. S.	Orient. O_1	Calculated Scattering ($H_2O=1$) Total C. S.	Comp. C.	Dens. D.	Orient. O.
1.271	1.00	.21	1.00	0	.79	0.21
1.317	1.43	.34	1.28	.198	.77	.31
1.353	1.60	.42	1.52	.369	.76	.39
1.427	2.17	.65	2.01	.702	.71	.60
1.443	2.30	.71	2.11	.766	.70	.65

Ba.—Barnes: "L. B. Tables", 408 (1923).
Di.—Dinkhauser: "L. B. Tables", 992 (1923).
Sw. and Ta.—Same as under earlier Tables.

Results in Table VIII and Graph 9 show: Fair agreement between the observed and calculated scattering; a large orientation scattering and a fairly large composition scattering for the higher concentrations.

Potassium Iodide.

Recipe for 54.90% solution in Table IX:

To a 750 cc. flask were added in order—

714 cc. of app. 55% potassium iodide (Kahlbaum's) solution,
25 cc. of app. 50% cadmium iodide (Baker's C.P.) solution,
11 cc. of app. 20% potassium hydroxide (Merck's) solution,

where these last two quantities were obtained by titrating in the presence of 55% potassium iodide solution, using phenolphthalein as indicator. This precipitate of cadmium hydroxide was not nearly as gelatinous as the aluminium hydroxide and settled down to the bottom of the flask, leaving practically all of the solution clear of precipitate.

TABLE IX

Potassium Iodide

%	S. G. $18°$ Get.	M	$\mu^{22°}_{D}$ Sw.	$\beta^{20°}_{10^6}$ 1-300 at. Gi.	$p^{mm.}_{100°}$ Ta.	ρ	ρ_1
0	1.000	0	1.3327	44.37	760.0	.109	.125
5.75	1.042	.361	.3410	43.28	752.2	.101	——
10.80	1.083	.705	.3485	42.32	743.5	.077	——
16.25	1.131	1.11	.3568	41.28	731.2	.059	——
21.70	1.182	1.55	.3661	40.20	717.0	.063	.094
31.10*	1.283	2.40	.3850	38.30	685.5	.064	——
39.00	1.381	3.25	.4012	36.70	652.0	.075	——
54.90	1.633	5.40	.4470	33.25	552.0	.078	083

	Observed Scattering ($H_2O=1$)		Calculated Scattering ($H_2O=1$)			
$\frac{6(1+\rho)}{6-7\rho}$	Total O. S.	Orient. O_1	Total C. S.	Comp. C.	Dens. D.	Orient. O.
1.271	1.00	.21	1.00	0	.79	.21
1.248	1.65	.30	1.69	.53	.81	.34
1.183	2.25	.35	2.01	.85	.8	.31
1.138	2.75	.33	2.22	1.06	.89	.27
1.148	3.42	.44	2.82	1.53	.93	.36
1.150	3.86	.50	3.73	2.22	1.02	.49
1.179	4.43	.67	4.28	2.52	1.11	.65
1.187	5.03	.79	5.24	3.04	1.37	.83

Get.—Getman: "L. B. Tables", 405 (1923).
Sw.; Gi.; Ta.—Same as under previous Tables.

* Duplicate solution gave $\frac{\%}{30.75}$ $\frac{\text{S. G.}}{1.279}$ $\frac{\text{Sc. } (H_2O=1)}{3.83}$ $\frac{\rho}{0.066}$

Results in Table IX and Graphs 2 and 10 show: For all concentrations, low values of ρ, for which there is a minimum value; good agreement between the observed and calculated relative scattering; a composition scattering which increases rapidly with concentration and a density scattering which shows fair increases with increase in concentration; the orientation scattering forms a negligible part of the total scattering in these solutions.

The irregularity of the calculated values in this case is due to two facts; first, the composition scattering is an unusually large fraction of the total scattering; second, this term contains the value $(\partial\mu^2/\partial x)^2$ which involves the square of a difference between the squares of the refractive indices for two solutions with small difference in composition. The difficulty of obtaining accurate values of $(\partial\mu^2/\partial x)$ is accentuated by the fact that μ^2 for this solution is very far from being a linear function of the concentration; an error of 1 in the fourth decimal place in the refractive index makes an error of 5% in the value of the composition scattering.

Ammonium Sulphate.

Recipe for the 42.30% solution, given in Table X:
To an 1100 cc. flask were added in order—

1025 cc. of app. 45% ammonium sulphate (Merck's C.P.) solution,
2 cc. of chlorine water containing 0.01 g. chlorine,
12 cc. of app. 28% ammonia (B. & A. C.P.),
45 cc. of app. 32% aluminium sulphate (Merck's) solution,

where these last two quantities were determined by titrating in the presence of 45% ammonium sulphate solution, using method previously described for ammonium salts.

TABLE X
Ammonium Sulphate

%	S. G. 15° Lu.	M	$\mu_D^{17.5^\circ}$ Wa.	$\beta^{20^\circ}_{.10^6}$ 1-300 at. Gi.	$p^{mm.}_{100^\circ}$ Ta.	ρ	ρ_1
0	1.000	0	1.3332	44.37	760.0	.109	.125
11.80	1.068	.95	.3520	38.75	736.0	.142	.376
20.85	1.120	1.77	.3662	34.40	713.3	.200	.560
33.12	1.189	2.98	.3855	28.65	673.0	.308	.694
42.30	1.242	3.98	.3995	24.15	629.0	.387	.664

	Observed Scattering ($H_2O=1$)		Calculated Scattering ($H_2O=1$)			
$\frac{6(1+\rho)}{6-7\rho}$	Total O. S.	Orient. O_1	Total C. S.	Comp. C.	Dens. D.	Orient. O.
1.271	1.00	.21	1.00	0	.79	.21
1.369	1.95	.53	2.39	.95	.80	.64
1.565	2.56	.92	3.22	1.26	.80	1.17
2.041	2.70	1.38	4.15	1.27	.77	2.12
2.528	3.10	1.87	4.13	.92	.72	2.50

Lu.—Lunge: "L. B. Tables", 390 (1923).
Wa.; Gi.; Ta.—Same as under previous Tables.

Results in Table X and Graph 11 show: Values of ρ that increase rapidly with concentration; values of observed scattering which are considerably lower than those caluclated from the Einstein formula, and a maximum for the composition scattering. It is also noted that the calculated values of total scattering reach a maximum at about 37.5%.

Note on solutions of the following salts of divalent metals—

The solutions of the following four salts, owing to the method of preparation, contained a small amount of sodium or potassium salt of the acid (referred to below as impurity). In order to minimize the effect of this additional salt the weaker solutions were made up by diluting the strong dust-free solution. This was accomplished by only partially displacing the dust-free water in the cross by the salt solution, homogeneity being obtained by gentle tipping[1] of the cross after permanent seals have been made. The ratio of salt to impurity, found by gravimetric analysis, is given under the individual salts. All data in Tables XI to XIV inclusive refer to the percent (given in Column 1) of salt under investigation, neglecting the small amount of added impurity, except the values of ρ and O.S. which are measurements of this solution plus the impurity. The work on the 3-component system (given later in this report) shows that these values are approximately additive, in which case the scattering due to the small amount of impurity may be safely neglected. This is also borne out by the results mentioned in the paragraph "Dust-free Salt Solutions", where a 10% excess of one of the reagents used for the precipitates had no measurable effect on the scattering.

Barium Chloride.

Recipe for the 22.26% solution given in Table XI:
To an 1100 cc. flask were added in order—
1070 cc. of app. 23% barium chloride (Baker's C.P.) solution,
2 cc. of chlorine water, containing 0.01 g. chlorine,
20 cc. of app. 10% sodium sulphate (Merck's) solution.
The ratio of barium chloride to impurity (in this case sodium chloride), as given by analysis, was 22.26% barium chloride to 0.10% sodium chloride.

TABLE XI

Barium Chloride

%	S. G. 15° Ge.	M	$\mu_D^{17.5^\circ}$ Wa.	$\beta_{.106}^{15^\circ}$ 1-10 at. Sch.	$p_{100^\circ}^{mm.}$ Ta.	ρ	ρ_1
0	1.000	0	1.3332	45.90	760.0	.109	.125
7.37	1.068	.379	.3446	43.22	747.2	.082	.109
11.38	1.108	.609	.3513	41.50	738.3	.069	——
13.44	1.130	.734	.3548	40.64	733.3	.064	.087
22.26	1.234	1.33	.3714	36.17	708.0	.061	.127

[1] Garrard: Proc. Roy. Soc. Canada, **18**, 126 (1924). Showed that shaking produces motes in the liquid.

TABLE IX continued

$\frac{6(1+\rho)}{6-7\rho}$	Observed Scattering ($H_2O=1$) Total O. S.	Orient. O_1	Calculated Scattering ($H_2O=1$) Total C. S.	Comp. C.	Dens. D.	Orient. O.
1.271	1.00	.21	1.00	0	.79	.21
1.196	1.59	.26	1.78	.67	.81	.29
1.162	2.19	.31	2.04	.93	.82	.29
1.150	2.36	.31	2.15	1.03	.83	.28
1.142	2.71	.34	2.72	1.54	.84	.34

Ge.—Gerlach: "L. B. Tables", 386 (1923).
Sch.; Wa.; Ta.—References same as under Table IV.

Results in Table XI and Graphs 1 and 12 show: Low values of ρ for all concentrations; good agreement between the calculated and observed scattering and a large composition scattering for the higher concentrations.

Calcium Chloride.

Recipe for the 33.70% solution in Table XII:
To an 1100 cc. flask were added in order—

708 cc. of app. 34% calcium chloride (Merck's) solution,
5 cc. of app. 5% mercuric chloride solution,
17 cc. of app. 16% aluminium chloride (Baker's C.P.) solution,
20 cc. of app. 15% sodium hydroxide (Merck's) solution,

where these last two quantities were obtained by titrating in the presence of 34% calcium chloride solution, using phenolphthalein as indicator. Ratio of salt to impurity was 33.70% calcium chloride to 0.30% sodium chloride.

TABLE XII

Calcium Chloride

%	S. G. 15° Ge.	M	$\mu_D^{17.5^\circ}$ Wa.	$\beta_{10^6}^{20^\circ}$ 2-20 at. Dr.	$p_{100^\circ}^{mm.}$ Ta.	ρ	ρ_1
0	1.000	0	1.3332	45.60	760.0	.109	.125
14.29	1.127	1.46	.3691	33.60	678.0	.154	.324
33.70	1.327	4.03	.4245	23.90	489.0	.230	.398

$\frac{6(1+\rho)}{6-7\rho}$	Observed Scattering ($H_2O=1$) Total O. S.	Orient. O_1	Calculated Scattering ($H_2O=1$) Total C. S.	Comp. C.	Dens. D.	Orient. O.
1.271	1.00	.21	1.00	0	.79	.21
1.406	2.45	.71	2.22	.81	.77	.74
1.681	3.33	1.35	2.92	.92	.82	1.18

Ge.—Gerlach: "L. B. Tables", 386 (1923).
Dr.—Drecker: Wied. Ann., **34**, 952 (1888).
Wa. and Ta.—Same as under Table IV.

Results for the calcium chloride solutions show: Fair agreement between O.S. and C.S.; larger ρ's and O's than found in any of the other chlorides; a composition scattering that reaches a maximum at about 28%.

Calcium Nitrate.

Recipe for the 37.11% solution in Table XIII:
To a 750 cc. flask were added in order—

720 cc. of app. 38% calcium nitrate (Baker's) solution,
2 cc. of chlorine water, containing 0.01 g. chlorine,
15 cc. of app. 28% aluminium nitrate (Merck's) solution,
13 cc. of app. 20% potassium hydroxide (Merck's) solution,

where these last two quantities were determined by titrating in presence of 38% calcium nitrate solution, using phenolphthalein as indicator. Ratio of salt to impurity was 37.11% calcium nitrate to 0.32% potassium nitrate.

TABLE XIII
Calcium Nitrate

%	S. G. $17.5°$ Ge.	M	$\mu_D^{25°}$ Sw.	$\beta_{.10^6}^{20°}$ 1-40 at. Sw.	$p_{100°}^{mm.}$ Ta.	ρ	ρ_1
0	1.000	0	1.3325	45.80	760.0	.109	.125
14.39	1.113	.98	.3350	39.18	724.4	.160	——
16.40	1.130	1.13	.3586	38.20	717.0	.186	.255
22.68	1.187	1.64	.3696	35.34	693.7	.244	.339
37.11	1.335	3.02	.3975	29.25	617.5	.352	.420

$\frac{6(1+\rho)}{6-7\rho}$	Observed Scattering ($H_2O=1$) Total O. S.	Orient. O_1	Calculated Scattering ($H_2O=1$) Total C. S.	Comp. C.	Dens. D.	Orient. O.
1.271	1.00	.21	1.00	0	.79	0.21
1.427	2.31	.69	2.46	.92	.81	.74
1.515	2.86	.97	2.73	.99	.81	.93
1.739	3.36	1.43	3.31	1.09	.81	1.41
2.294	4.10	2.41	4.22	1.01	.83	2.38

Ge.—Gerlach: "L. B. Tables", 386 (1923).
Sw. and Ta.—Same as under previous Tables.

Results for the calcium nitrate solutions show: Very good agreement between the observed and calculated scatterings; large values of ρ and a composition scattering that reaches a maximum at about 29%.

Lead Nitrate.

Recipe for 24.33% solution in Table XIV:
To an 1100 cc. flask were added in order—

1080 cc. of app. 25% lead nitrate (de Haen) solution,
20 cc. of app. 10% sodium sulphate (Merck's) solution,

this volume of sodium sulphate solution being sufficient to produce about 5 g. of lead sulphate precipitate. Ratio of salt to impurity was 24.33% lead nitrate to 0.21% sodium nitrate.

TABLE XIV
Lead Nitrate

%	S. G. 17.5° Ge.	M	$\mu_D^{25^\circ}$ Sw.	$\beta^{20^\circ}_{.10^6}$ Sw.	$p^{mm.}_{100^\circ}$ Ta.	ρ	ρ_1
0	1.000	0	1.3325	45.80	760.0	.109	.125
5.40	1.047	.171	.3389	44.80	755.5	.079	.107
11.01	1.101	.366	.3460	43.62	750.5	.077	.104
14.84	1.141	.512	.3512	42.72	747.0	.071	.098
24.33	1.252	.920	.3651	40.25	736.3	.063	.092

	Observed Scattering ($H_2O=1$)		Calculated Scattering ($H_2O=1$)			
$\frac{6(1+\rho)}{6-7\rho}$	Total O. S.	Orient. O_1	Total C. S.	Comp. C.	Dens. D.	Orient. O.
1.271	1.00	.21	1.00	0	.79	.21
1.189	1.85	.29	1.77	.68	.81	.28
1.183	3.14	.48	2.68	1.43	.84	.41
1.168	4.55	.65	3.34	2.00	.86	.48
1.148	6.30	.81	4.73	3.22	.90	.61

Ge.—Gerlach: "L. B. Tables", 390 (1923).
Sw. and Ta.—Same as under previous Tables.

Results in Table XIV and Graphs 1 and 15 show: Low values of ρ; observed scattering values higher than the calculated values; a composition scattering that increases rapidly with concentration forming for the higher concentrations the larger part of the total scattering.

Hydrogen Chloride.

The hydrogen chloride solutions were prepared dust-free by the "Distillation in Vacuo" method, using Baker's C.P. acid. Results follow in Table XV.

TABLE XV
Hydrogen Chloride

%	S. G. 15° C. H.	M	$\mu_D^{25^\circ}$ Sw.	$\beta^{20^\circ}_{.10^6}$ Sw.	30° Part. Press Ra.	ρ	ρ_1
0	1.000	0	1.3325	45.80	33.0	.109	.125
7.15	1.035	2.03	.3495	43.42	15.3	.127	.127
11.78	1.058	3.41	.3608	42.33	9.0	.132	.133
21.92	1.110	6.66	.3856	40.58	4.6	.178	.178
24.97	1.126	7.70	.3928	40.15	6.7	.182	.182

	Observed Scattering ($H_2O=1$)		Calculated Scattering ($H_2O=1$)			
$\frac{6(1+\rho)}{6-7\rho}$	Total O. S.	Orient. O_1	Total C. S.	Comp. C.	Dens. D.	Orient. O.
1.271	1.00	.21	1.00	0	.79	.21
1.323	1.36	.33	1.19	.03	.87	.29
1.339	1.60	.40	1.31	.05	.93	.33
1.487	1.70	.56	1.74	.11	1.06	.57
1.501	1.80	.60	1.80	.09	1.10	.60

C. H.—"Chemists Handbook", 293 (1919).
Sw.—Same as under earlier Tables.
Ra.—Rayleigh: "Scientific Papers", **5**, 79; Dolezalek: Z. physik. Chem., **26**, 334 (1898)

Results in Table XV and Graph 16 show: Poor agreement for the low concentrations and good agreement between the calculated and observed scattering for the high concentrations; low values for the composition scattering which becomes zero at about 18%, due to $\partial p_{mm}/\partial x$ being zero at this concentration; a large density scattering and a fairly low orientation scattering. The composition scattering could be calculated only very roughly with the available data of Rayleigh and Dolezalek.

Acetic Acid.

The acetic acid solutions were prepared dust-free by the "Distillation in Vacuo" method, using Grasselli's C.P. acid. Results are given in Table XVI.

TABLE XVI

Hydrogen Acetate

%	S. G. 15° Ou.	M	$\mu_D^{20°}$ Bu.	$\beta_{.10^6}^{25°}$ Dr.	100° Par. Press. H_2O Ra	ρ.	ρ_1
0	1.000	0	1.3331	47.0	760.0	.109	.125
14.00	1.020	2.38	.3434	45.8	728.0	.171	.171
23.46	1.033	4.04	.3495	45.1	702.0	.224	.224
39.67	1.052	6.95	.3605	45.5	650.0	.281	.281
62.60	1.070	11.16	.3736	53.4	537.0	.356	.356
80.00	1.075	14.34	.3772	68.8	380.0	.408	.408
98.59	1.059	17.40	.3726	96.0	25.0	.423	.423

	Observed Scattering ($H_2O=1$)		Calculated Scattering ($H_2O=1$)			
$\frac{6(1+\rho)}{6-7\rho}$	Total O. S.	Orient. O_1	Total C. S.	Comp. C.	Dens. D.	Orient. O.
1.271	1.00	.21	1.00	0	.79	.21
1.463	2.04	.65	1.48	.180	.84	.46
1.657	2.43	.96	1.91	.283	.87	.76
1.905	3.04	1.44	2.38	.290	.96	1.13
2.319	3.74	2.13	3.01	.064	1.24	1.71
2.686	5.07	3.18	4.39	0	1.63	2.76
2.809	6.90	4.44	6.18	0	2.20	3.98

Ou.—Oudemans: "Chemists Handbook", 290 (1919).
Bu.—Buchkremer: "L. B. Tables", 991 (1923).
Dr.—Drecker: "L. B. Tables", 101 (1923).
Ra.—Rayleigh: "Scientific Papers", 5, 76.

Results in Table XVI and Graph 17 show: Calculated values of scattering lower than the observed values by an approximately constant figure; a small composition scattering which for an 80% solution becomes zero, due to a maximum of μ at that concentration; a rapid increase in the orientation scattering with concentration, and a fairly rapid increase in the density scattering with concentration for the higher concentrations.

Additional Results

Measurements were made on solutions of sulphuric acid (Baker's C.P.) and nitric acid (B. & A. C.P.), prepared dust-free by the "Distillation in Vacuo" method. No calculations were made for these solutions. Results follow in Table XVII.

TABLE XVII
Acids

Solute	%	S. G. 15°	ρ	ρ_1	Observed Scattering ($H_2O = 1$) Total O. S.	Orient. O_1
Hydrogen sulphate	92.70	1.832	.341	.341	2.16	1.09
Hydrogen nitrate	75.46	1.433	.590	.590	5.98	4.81

The value of ρ for 75.46% HNO_3 solution is remarkably high, although it is to be noted that if the graphs for the nitrate solutions of sodium and ammonium are extrapolated to this percentage, a value ρ of approximately the same order of magnitude is obtained. In both solutions the orientation scattering forms the greater part of the total scattering.

General Conclusions.

The agreement between the total observed and the total calculated relative scattering is quite good for all the solutions measured, with the exception of the solutions of acetic acid and lead nitrate, where the observed values are higher than the calculated, and the solutions of ammonium sulphate where the observed values are much lower than the calculated.

The density scattering is the only part of the total scattering remaining practically constant in all cases, with the exception of the acetic acid solutions above a 60% concentration, where there is a rapid increase in the density scattering with increase in the concentration of the solution. The density scattering is the most important factor in the total scattering when the total scattering is small (see results for chlorides of Na, K and NH_4).

The composition scattering is the most variable part of the total scattering and shows: Very large increases with concentration in the solutions of potassium iodide, lead nitrate, and barium chloride; fair increases with concentration in the solutions of calcium chloride, calcium nitrate and sodium sulphate; small increases with concentration in the solutions of potassium nitrate, sodium nitrate, ammonium nitrate and ammonium chloride; very small increases with concentration for the acids (acetic and hydrochloric), giving in both cases a maximum and then a zero value; a maximum for the solutions of sodium chloride and potassium chloride (where the increases are relatively small) and for the solutions of ammonium sulphate (where the increases are relatively large).

The orientation scattering increases with concentration in all the solutions, showing most rapid increases where the formula of the salt is complex

(nitrates, sulphates and acetates), and least increases where the formula of the salt is simple (chlorides and iodides of monovalent cations), while in the case of the chlorides of the divalent metals these increases are variable.

In general it is noted from these results that the salts fall into groups, where the members of a group show similar features; this is noted in the chloride group of Na, K and NH_4, the nitrate group of the same cations, and the "heavy" group of lead nitrate, potassium iodide and barium chloride.

Molecular Anisotropy.

If the orientation scattering is attributed to the random orientation of anisotropic molecules the unpolarized part of the total scattering, and approximately, therefore, the orientation scattering, would be proportional to the number of molecules, n_1 and n_2, of each kind per unit volume of solution[1] or $O_1 = n_1X_1 + n_2X_2$, where X_1 and X_2 are constants characteristic of each salt. If, further, the X_2 for the water is assumed to be unaffected by the presence of the salt, the orientation scattering of equimolar solutions of different salts, less the orientation scattering of water, would be a measure of the value of X_1 for the various salts studied.

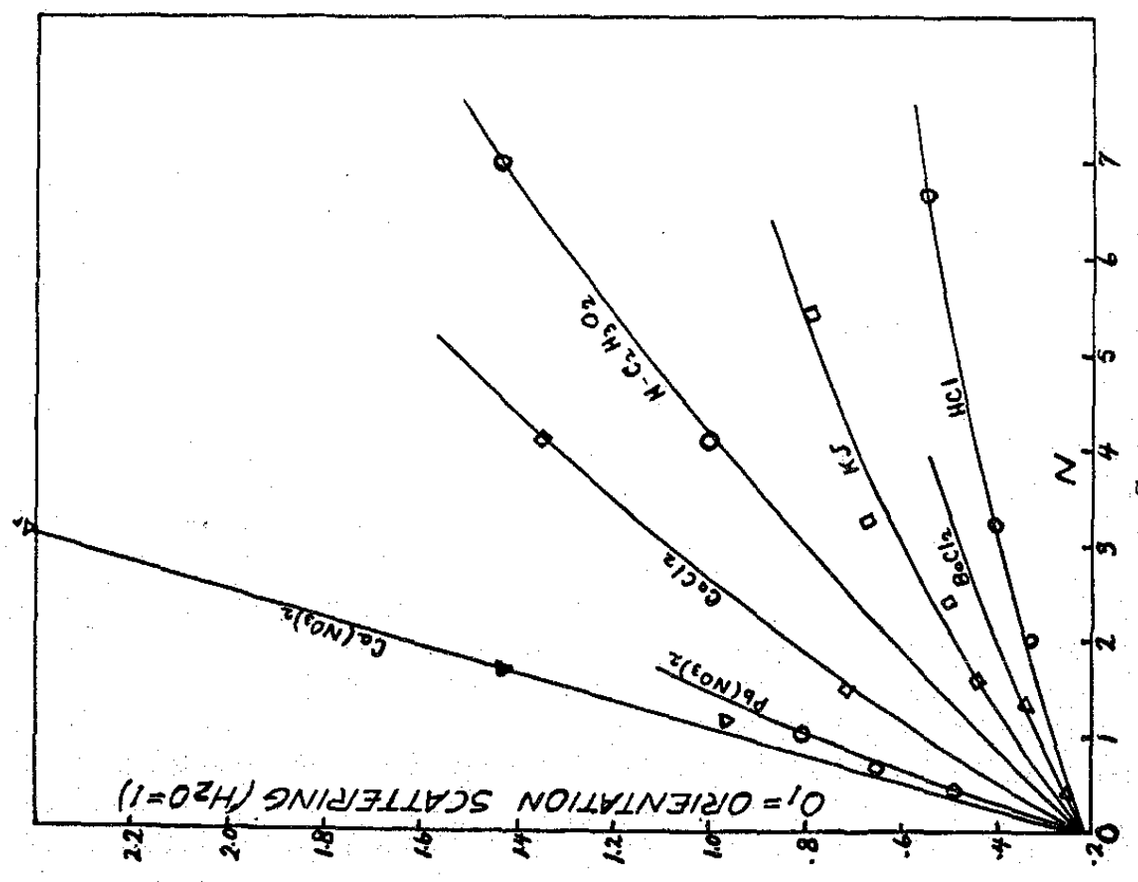
In Graphs 18 and 19 the values plotted are those given in the Tables under the columns M and O_1. These graphs show that the orientation scattering, calculated from the observed total scattering and the depolarization factor, is in most cases approximately a linear function of the volume concentration of the salt. It is noted further from results plotted in Graph 18, that the values of the orientation scattering for the same molar concentrations fall into distinct groups, the chlorides of three univalent cations having the lowest values, the nitrates greater values and the sulphates still greater values. The order of the cations within the chloride and nitrate groups is the same, namely, in increasing order, potassium, sodium and ammonium. This is also true of the sulphate group, if the calculated values for the total scattering are taken for the ammonium sulphate, which is the only case where there was a great divergence between the calculated and observed total scattering.

The curve for HCl on Graph 19 evidently falls into the chloride group on Graph 18, in which group the KCl has the lowest values, while the nitrates of the two divalent metals, calcium and lead have the highest values of any measured. The orientation scattering is thus seen to be in accord with other properties of aqueous salt solutions in respect to additivity.

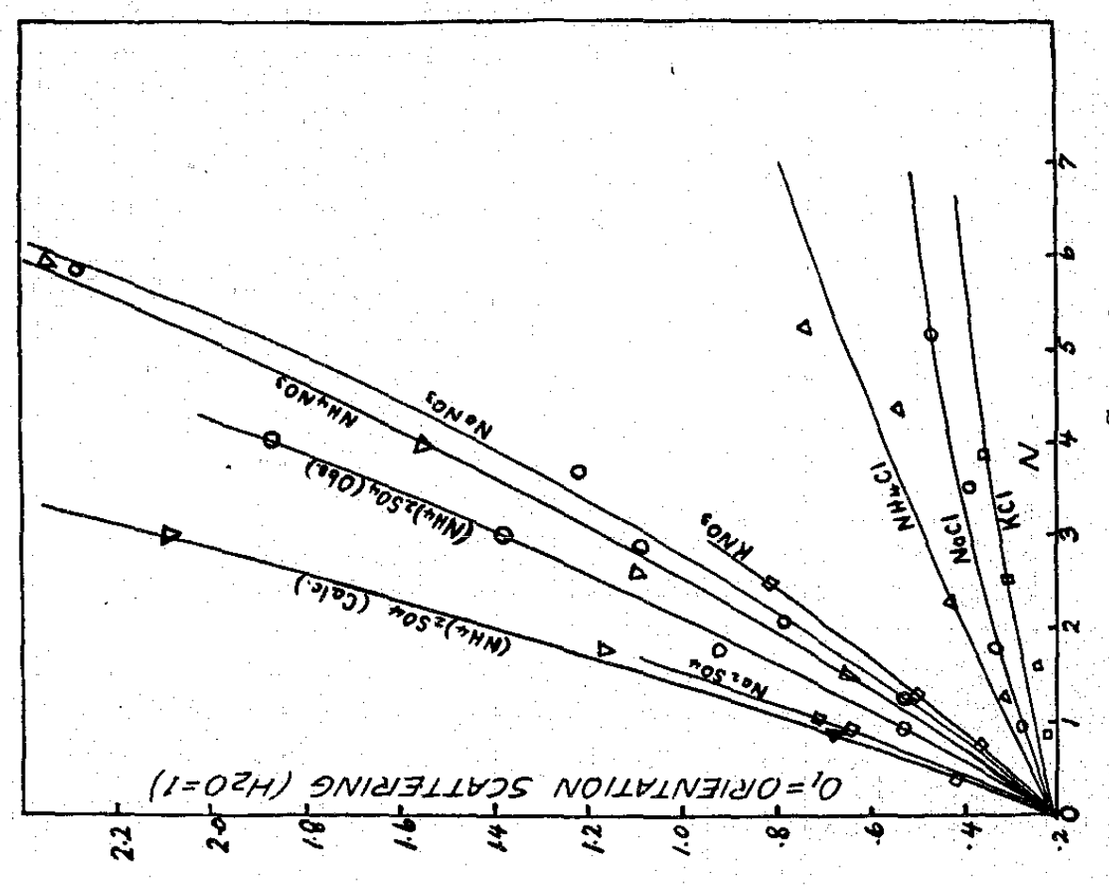
Systems of more than two Components.

A preliminary study of the light scattering in solutions containing two or more salts was made. Results were obtained for a solution of sodium chloride and sodium nitrate having a common ion, and for a solution of sodium nitrate and potassium chloride with no common ion. The solutions were obtained dust-free in crosses by following the same procedure described in the section "Technique", except that when the cross was half full of one

[1] Raman: Phil. Mag., 45, 220 (1923)



GRAPH 19



GRAPH 18

solution it was transferred to the other flask of dust-free solution. Before measurements were made gentle tipping brought homogeneity to the mixture. The composition, as before, was found by analysis, after all readings had been taken. The results are given in Table XVIII.

To calculate the light scattering by the Einstein-Smoluchowski method strictly would involve an additional "composition term" for the salts with a common ion and three for the salts without a common ion. For these the data are not available and would be very difficult to obtain. As a makeshift, calculations were made for the two solutions in which the total salt was treated as a single salt. The compressibilities, refractive indices, and vapour pressures were determined for the solutions measured; and the latter two properties were determined also for solutions of higher and lower total concentrations in order to obtain values for $\partial\mu^2/\partial x$ and $\partial p_2/\partial x$. These data and the calculated light scattering are given in Table XVIII. The values calculated in this way might be expected to give results too low and as a matter of fact, the small deviations of the observed from the calculated relative scatterings are in this direction.

The scattering may also be calculated from the observed scattering of the individual salts, on the assumption that the values are additive.

TABLE XVIII

Total %	S. G. 20°	$\beta^{20°}_{.10^6}$ 1-40 at.	$\mu^{25°}_D$	B.Pt 760 mm.	mm. $p_{100°}$	Light Scattering ($H_2O=1$)	
						Observed	Calculated
0	1.000	45.80	1.3325	100.00°	760.0	1.00	1.00
10.75	——	——	1.3488	101.70	715.0	2.08	2.02
21.50*	1.160	32.91	1.3648	104.04	653.1	2.10	1.81
32.25	——	——	1.3832	107.42	563.7		
20.32	——	——	1.3595	102.93	682.5		
25.40†	1.180	32.99	1.3663	103.90	656.9		
30.48	——	——	1.3736	105.27	620.6		

ρ	ρ_1
.109	.125
.238	.340
.184	.262

*Contained 10.81 X sodium chloride and 10.69 X sodium nitrate.
†Contained 14.54 X Potassium chloride and 10.86 X sodium nitrate.

The value for the sodium chloride—sodium nitrate solution computed from the interpolated values for 10.81% NaCl (1.33) and 10.69% $NaNO_3$ (1.63), less 1.00, is 1.96, which is 6% less than the observed value (2.08); for the KCl-$NaNO_3$ solution this additive value (1.38+1.64−1.00) is 2.02, 4% less than the observed value of 2.10. The approximate additivity of the light scattering indicated by these results justified our previous assumption in the case of the divalent metals that the small amount of "impurity" (a second salt) would have no measurable effect on the measurement.

Fluorescence

One of the factors which caused error in my first measurements on light scattering (see introduction) was the fluorescence present in the solutions. This is now eliminated by the use of a quinine sulphate filter which cuts off all the ultra-violet light from the incident beam. One method of making a quantitative determination of this fluorescent light in the solutions when the light scattering is being observed would be to measure the relative light scattering, first with the quinine filter in the path of the incident beam and then after the filter had been removed, the difference in the readings being a measurement of the fluorescence present. The method actually used by the author, however, proved to be not only a simpler but a more accurate one.

As stated earlier in this paper, the measurement of ρ determines the ratio of the intensity of the weak to the strong component of polarization. Then, knowing the relative intensity of the sum of these two components (i.e. the relative light scattering of any solution), we can determine the intensity of the two components separately (relative to $H_2O=1$). Fluorescent light is unpolarized. Therefore, the addition of fluorescent light to the total scattering means the addition of equal portions to the two components, and consequently from a measurement of the depolarization factors with and without the quinine filter the fluorescent light present in the solution can be found. This was the purpose of the measurements of ρ_1 given in earlier Tables.

If we denote the unpolarized scattered light by A and the polarized by B, then $\rho = A/B$, and (A+B) = the total intensity of the scattered light. From these relations we can calculate A and B. In the case of a solution showing signs of fluorescence the value of ρ is increased by the addition of fluorescent light, or, denoting the relative intensity of the fluorescent light by 2X, we may write

$$\frac{A+X}{B+X} = \rho_1 \text{ or } X = \frac{\rho_1 B - A}{1-\rho_1}$$

Knowing A and B we can find 2X for any solution measured. In Table XIX are given the results for a few typical cases, where 2X is a relative value (light scattering of water = 1). The values of ρ and ρ_1 used, were taken from previous Tables.

TABLE XIX

Solute or liquid	Relative Scattering ($H_2O=1$)				
	%	A	B	A+B	2X
Water	0	.10	.90	1.00	.03
Methyl Alcohol	0	.27	2.50	2.77	0
Hydrogen Chloride	7.15	.15	1.21	1.36	0
" "	11.78	.19	1.41	1.60	0
All Acids	of any % gave $2X=0$				
Potassium Chloride	6.12	.10	1.02	1.12	.09
" "	11.04	.11	1.18	1.29	.17
" "	17.00	.14	1.37	1.51	.36
" "	24.60	.17	1.48	1.65	.30
Ammonium Chloride	6.67	.14	1.15	1.29	.31
" "	11.67	.20	1.56	1.76	.66
" "	22.00	.25	1.87	2.12	.55
" "	26.00	.34	2.21	2.55	1.14
Ammonium Sulphate	11.80	.24	1.71	1.97	1.29
" "	20.85	.43	2.13	2.56	3.47
" "	33.12	.63	2.07	2.70	5.27
" "	42.30	.87	2.23	3.10	3.65
Lead Nitrate	5.40	.14	1.71	1.85	.11
" "	11.01	.22	2.92	3.14	.19
" "	14.84	.30	4.25	4.55	.26
" "	24.33	.37	5.93	6.30	.39

It is obvious from the above results that this method of determining fluorescence will give a measure of a fluorescence so faint as to be within the experimental error of intensity readings, as in the case of water.

The conclusions[1] reached were:

(1) Acid solutions show no signs of fluorescence.

(2) Water shows signs of fluorescence, although this is very small (3% of total scattering). In an attempt to get rid of this fluorescence, water was boiled in a distillation apparatus for 3/4 of an hour before it was evacuated and sealed off. When dust-free it was measured immediately, but approximately the same amount of fluorescence was observed. In a second attempt to get rid of this fluorescence, a distillation apparatus as before was used, the water being slightly acidic (N/20 hydrochloric acid). No difference could now be observed between ρ and ρ_1; any difference now being within the experimental error of such readings. Water was also prepared dust-free in a silica distillation apparatus and silica cross, but no decrease in the amount of fluorescence was observed.

[1] Since the above was written some observations have been made directly with an intense arc beam focussed in the liquid, with nearly all the visible light cut out by a "red-violet" nickel-glass plate. By this method even acids and acidulated water showed a slight fluorescence. It must be further noted that the values in table XIX for 2X are all slightly too low and should be divided by an unknown factor a little less than unity, representing the extinction coefficient and reflection of the quinine cell which unfortunately were not determined. This omission, of course, will not affect any of the other results. (F. B. K. May, 1927).

(3) All the salt solutions showed fluorescence, but this was especially high in the case of ammonium chloride and sulphate, the latter solutions especially giving values which changed very irregularly with the concentration.

A solution of 26% ammonium chloride, prepared from Merck's stock supply, gave an extremely high fluorescence ($\rho_1 = .790$), while that given by Kahlbaum's salt is the value given in Table XIX. Recrystallization of Kahlbaum's salt three times did not decrease this fluorescence value, showing that probably a part of the total fluorescence was due to impurities added with the reagents used in forming the precipitate (ammonia and aluminium chloride). Tests by recrystallizing four times Merck's ammonium sulphate showed a large decrease in the fluorescence values given in Table XIX, these being reduced to the same order as those for Kahlbaum's ammonium chloride (Table XIX). This shows that a large part of the fluorescence is due to impurities in the ammonium salt which can be removed by crystallization.

The fact that the greatest irregularity in the values was observed in the solutions in which two reagents were added to make the precipitate, suggests that the fluorescence may be dependent on slight deviations from the neutrality of the solutions. Solutions of ammonium sulphate, to which sulphuric acid was added, still showed much fluorescence, but as these solutions were not dust-free, the results are not conclusive.

Although the amount of fluorescence varied with the purity of the salt, the measurements of the depolarization factor and of light scattering with the quinine sulphate cell always gave consistent results.

Compressibilities and Refractive Indices

Some of the data required in the calculations on light scattering, especially data on compressibilities and refractive indices, were either lacking or inadequate. In these cases the author made the required measurements.

Compressibilities Apparatus: The apparatus made of Pyrex glass shown in Fig. 5 consists of—

The *compression* chamber (P), having a volume from the end (L_1) to the top of the scale (S) of 55.94 cc. at 20°C. This chamber was filled by applying a slight suction at L_2 and drawing in the liquid at L_1. The same outlets were used for emptying, rinsing and drying the chamber. The uniformity and volume of the compressibility capillary (S) was found by weighing a mercury thread; the bore was uniform, having a volume of 0.108 cc. per cm. of length. A steel cm. scale (S) was attached to this capillary. The expansion of the compression chamber was found by measuring the compressibility of mercury at the pressure and temperature subsequently used (40 atmos. and 20°C.); this expansion was .0308 cc.

The *Manometer* M_1 consisting of a vertical capillary and the bulbs B_2 and B_3. The bulb B_2 was larger than B_3 and slightly lower, being nearly filled with mercury. When the pressure was applied the mercury was forced into B_3 and at the point 40 on the vertical scale, the volume of the air in the manometer was 1/40 of the original volume, indicating a pressure of 40 at.

The *Pressure machine* used was a Fritz Köhler compression machine capable of giving pressures up to 100 at. This was attached to the apparatus by a sealing wax seal (C.) A finely drawn capillary in the form of a loop took up any jars incidental to the work. T′ and T″ etc. were suitably placed Tee's for filling the apparatus. O was the oil-water chamber, water being the medium used from O to the mercury level in B_1.

The temperature, 20°C., was kept constant to within 1/2°. The results are given in Table XX.

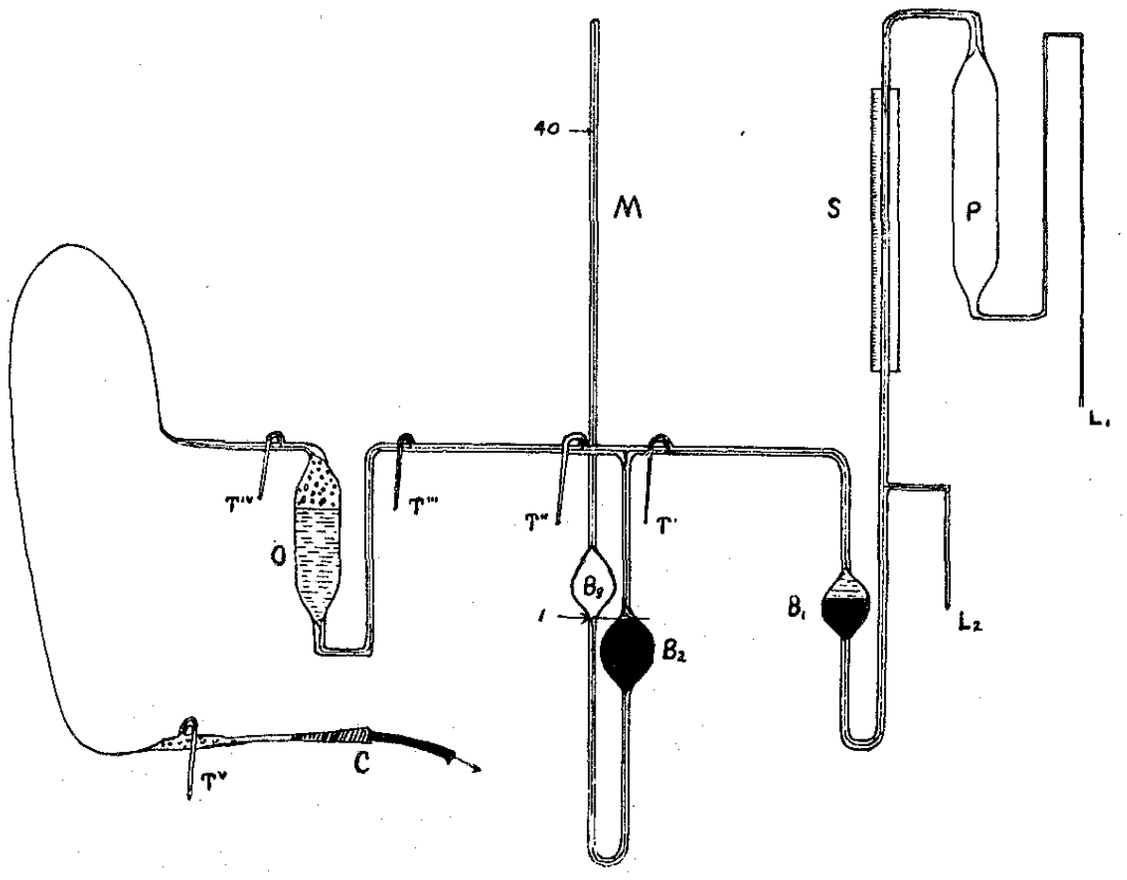


FIG. 5

Refractive Indices.

The refractive indices given in Table XX were obtained by use of a Pulfrich Refractometer. All results were made for sodium yellow light, at a temperature of 25°C., kept constant to 1/10°C.

Analysis in all cases was made by using a pyknometer and specific gravity tables.

TABLE XX

% = g. Anhydrous salt per 100 g. solution

Solute	%	S. G. $t°/t°$	$\beta^{20°} \times 10^6$	$\mu_{D.}^{25°C}$
Calcium Nitrate	0	1.000(17.5°C.)	45.80	1.3325
,,	10.23	1.076	41.46	.3482
,,	20.20	1.163	37.02	.3653
,,	29.37	1.253	31.68	.3830
,,	38.13	1.347	28.68	.3995
,,	47.10	1.447	25.17	.4186

TABLE XX (cont'd)

Solute	%	S. G. t°/t°	$\beta^{20°} \times 10^6$	$\mu_{D.}^{25°C}$
Lead Nitrate	11.07	1.095(17.5°C.)	43.99	
"	20.85	1.198	40.83	
"	31.40	1.331	38.33	
"	39.00	1.442	34.62	
Ammonium Nitrate	11.10	1.046(17.5°C.)	42.27	1.3470
"	20.38	1.086	39.32	.3589
"	30.36	1.131	35.53	.3723
"	40.50	1.180	32.81	.3871
"	49.75	1.227	29.05	.4007
Potassium Nitrate	5.65	1.036(15°C.)	43.40	
"	10.54	1.069	41.41	
"	18.68	1.126	37.47	
Sodium Sulphate	10.02	1.093(17.5°C.)	37.25	
"	15.25	1.145	33.22	
Hydrogen Chloride	12.19	1.060(15°C.)	42.27	1.3615
"	23.44	1.118	40.33	.3893
"	35.57	1.181	38.96	.4181
Sodium Nitrate	10.80	1.074(20°C.)		1.3451
"	19.55	1.140		.3557
"	29.25	1.220		.3672
"	35.25	1.273		.3750
"	40.32	1.322		.3817
"	45.50	1.374		.3890
Potassium Iodide	10:15	1.078(18°C.)		1.3474
"	20.39	1.169		.3637
"	30.36	1.274		.3835
"	40.38	1.398		.4045
"	50.00	1.547		.4318
"	57.00	1.672		.4539
Lead Nitrate	6.90	1.056(17.5°C.)		1.3408
"	11.06	1.095		.3461
"	16.18	1.146		.3530
"	21.70	1.208		.3613
"	26.06	1.260		.3680
"	31.04	1.326		.3772
"	37.50	1.421		.3898

The accuracy of the compressibility measurements as judged by the graphs plotted and by the readings on the standards (methyl alcohol and water after calibration with mercury) was within 2% for the most divergent cases.

These values were accurately plotted and values interpolated from these graphs were used in the calculations (see data in Tables by Sw.).

Summary

(1) Aqueous solutions of a wide range of salts have been prepared dust-free and their relative light scattering and depolarization factor measured.

(2) A technique has been devised whereby the solutions prepared dust-free can be transferred to glass crosses for quantitative measurements.

(3) An apparatus for the quantitative measurement of the light scattering and the depolarization factor is described.

(4) The results of the relative light scattering calculated from the Einstein-Smoluchowski-Cabannes formula show on the whole good agreement with the observed values.

(5) The orientation scattering was found to be approximately proportional to the molar concentration of the salt. The values of the orientation scattering for the same molar concentrations fall into distinct groups, the chlorides of three univalent cations having the lowest values, the nitrates greater values and the sulphates still greater values. The order of the cations within the chloride and nitrate groups is the same, namely, in increasing order, potassium, sodium and ammonium. This is also approximately true of the sulphate group.

(6) The relative scattering of solutions containing two salts is approximately that calculated on the assumption of additivity, and differs little from that calculated by the Einstein formula in which the solute is treated as a single salt.

(7) Water and salt solutions show fluorescence, a large part of which in the case of the solutions is shown to be due to impurities. Very little fluorescence was observed in the acid solutions.

(8) Measurements of the compressibilities and refractive indices of the solutions, for which no data were given in the literature, were made.

This research was carried out at the suggestion and under the direction of Professor F. B. Kenrick.

Toronto.
March, 1927.

THE RATE OF TRANSFORMATION OF ACETYLCHLOROAMINOBENZENE INTO *O*- AND *P*-CHLOROANILIDES AS A MEASURE OF THE CATALYTIC POWER OF THE HYDROCHLORIC ACID.

BY FREDERICK GEORGE SOPER

The study of the transformation of acetylchloroaminobenzene to *o*- and *p*-chloroacetanilides, under the influence of hydrochloric acid as catalyst, is of importance in the theory of strong electrolytes and reaction velocity and has been undertaken by Rivett[1], by Harned and Seltz[2] and by Åkerlof.[3] The measurement of the rate at which the chloroamine was transformed was based on the fact that acidified potasssium iodide reacts quantitatively with a chloroamine with formation of iodine, whilst no iodine is liberated by the nuclear chlorinated anilide. It will be shown that, owing to an overlooked factor, the results obtained for the rate of transformation when using the above method of analysis indicate a catalytic activity of the hydrochloric acid which is too high for the more concentrated solutions.

The main essential features of the transformation were demonstrated by Orton and Jones[4]. It was shown that the production of free chlorine was an intermediate step in the reaction which was completed by extra-nuclear chlorination of the acetanilide, the successive stages being symbolised—

$$C_6H_5NClAc + HCl \xrightarrow{A} Cl_2 + C_6H_5NHAc \xrightarrow{B} C_6H_4\begin{matrix}NHAc\\Cl\end{matrix} + HCl.$$

Since no indication of successive reactions can be observed from a study of the composition-time curve, it followed as a necessary corollary to the above mechanism that the velocity coefficients of the two stages had very different values, the rate being entirely governed by the slowness of either the first or the second of these successive reactions.[5] Which reaction actually governed the speed in aqueous media was not definitely settled.

It is now possible from a knowledge of the rate of formation of acetylchloroaminobenzene from acetanilide and chlorine, the determination of which is described below, combined with that of the equilibrium constant of the reaction: $Cl_2 + C_6H_5NHAc \rightleftarrows C_6H_5NClAc + HCl$, to show that the velocity coefficient of the interaction of acetylchloroaminobenzene with hydrochloric acid agrees with that of the transformation. The first of the above consecutive reactions therefore governs the rate of the transformation and is

[1] Z. physik. Chem., **82**, 201; **85**, 113 (1913).

[2] J. Am. Chem. Soc., **44**, 1476 (1922).

[3] Medd. Nobel Inst., **6**, No. 2, 1 (1925).

[4] Brit. Ass. Reports, **1910**, 85.

[5] The formation of chlorine from a chloroamine and hydrochloric acid does not involve preliminary hydrolysis of the chloroamine to hypochlorous acid since phenol which reacts rapidly with hypochlorous acid does not react to an appreciable extent with the chloroamine in aqueous solution at 25° in an examined period of seven hours. The rate of hydrolysis of the chloroamine in aqueous solution is therefore relatively slow.

the slow stage. The addition of readily chlorinatable substances, e.g., acetanilide, should not therefore alter the rate of fall of titre of the system.

Actually[1] an increase in the velocity was observed.

This apparently conflicting observation is due to the fact that in the mixture of chloroamine and hydrochloric acid, the chlorine when formed undergoes two main simultaneous reactions, (a) with the acetanilide forming *o*- and *p*-chloroanilides and (b) with the chloroanilides, which are present at a much higher concentration than acetanilide, forming chloroamines. These chloroamines of the chloroanilides are formed progressively and since they contribute to the iodine titre, the observed rate of fall of iodine titre is less than that of the formation of chlorine in reaction A. When excess of some readily *C*-chlorinatable substance is present competition for the chlorine reduces the *N*-chlorination of the chloroanilides to a negligible amount and the rate of fall of titre increases to a constant value equal to that of the formation of chlorine. The ratio in which the chlorine reacts to form *N*- and *C*-chlorinated products varies with the strength of the hydrochloric acid, being respectively less in the concentrated acid solutions owing to attainment of the equilibria: $C_6H_4\langle^{NHAc}_{Cl} + Cl_2 \rightleftarrows C_6H_4\langle^{NClAc}_{Cl} + HCl$. Since the true "catalytic" activity of the hydrochloric acid is measured by its rate of interaction with acetylchloroaminobenzene to form chlorine, the velocity determinations should be made in the presence of excess of substances which can remove the chlorine completely as formed. Suitable substances are acetanilide, phenol, and p-cresol. Results obtained at 25° using 0.2, 0.4, and 0.8 molal solutions of hydrochloric acid are given in Table 1.

TABLE I

Velocity coefficients of the transformation at 25.0°

Concentration of HCl	0.2	0.4	0.8M
$k = \frac{1}{t}\log_{10}\frac{a}{a-x}$	0.00172	0.00666	0.0282
k′ in presence of excess acetanilide, phenol, or *p*-cresol	0.00188	0.00711	0.0291
Ratio k/k′	0.915	0.937	0.970

These results show that the catalytic activity of the hydrochloric acid given by the rate of formation of chlorine is not proportional to the velocity coefficient, k, of the transformation as ordinarily measured. Such measurements contain a varying error indicating a catalytic activity which is, for example, 0.915 of the true value in 0.2 M HCl and 0.970 of the true value in 0.8 M HCl. Deductions based on such measurements lead to a relative catalytic activity of the 0.8 M HCl which is some 6% too high in comparison with that of the 0.2 M HCl. Before attempting to correlate the thermodynamic activity of the hydrochloric acid with new measurements of its catalytic activity, other factors are being investigated.

[1] Orton and Jones: Brit. Ass. Reports, **1910**, 85.

§ 2. Test of the mechanism of the transformation.

Calculation of the speed of interaction of acetylchloroaminobenzene with hydrochloric acid. The velocity coefficient, k_1, of the interaction of acetylchloroaminobenzene with hydrochloric acid can be expressed in terms of the equilibrium constant of the reaction, $C_6H_5NClAc + HCl \rightleftarrows C_6H_5NHAc + Cl_2$, and the velocity coefficient, k_2, of the formation of acetylchloroaminobenzene from acetanilide and chlorine. The equilibrium constant of the reaction can be deduced from the hydrolysis constant, K_h, of the chloroamine[1] and that of chlorine,[2] K_J, Thus

$$k_1/k_2 = [Cl_2]\,[C_6H_5NHAc] \,/\, [C_6H_5NClAc]\,[H^{\cdot}, Cl'] = \frac{[C_6H_5NHAc]\,[HOCl]}{[C_6H_5NClAc]} \,/\, \frac{[HOCl]\,[H^{\cdot}, Cl']}{[Cl_2]} = K_h/K_J \qquad (1)$$

The results of the measurements of the velocity coefficient, k_2, of the formation of the chloroamine of acetanilide and those of *o*- and *p*-chloroacetanilides are given in Table II.

TABLE II

Velocity coefficients of *N*- and *C*- chlorination at 25.0°

	C_6H_5NHAc	$C_6H_5\langle^{NHAc}_{Cl(4)}$	$C_6H_5\langle^{NHAc}_{Cl(2)}$
Chloroamine formation, k_2,	1.3×10^2	1.9×10^2	6.1×10^2
Nuclear chlorination, k_{ii},	1.7×10^4	2.1×10^2	45.

Substituting for k_2 in (1) the value 130, for K_h the value 7.3×10^{-7} and for K_J 4.84×10^{-4} one obtains $k_1 = 0.197$. The observed value in 0.8 *M* acid where the activity is 0.40, is $0.0291/\log_{10} e$, giving a value at unit acid activity of 0.17. These values are in satisfactory agreement.

The calculated value of the velocity coefficient of the transformation assuming that the second of the consecutive stages is the slower can be shown to be $k = k_{ii}K_h/K_J$, where k_{ii} is the velocity coefficient of nuclear chlorination of acetanilide, yielding a value some 130 times too great. The observed speed of the transformation is thus in satisfactory agreement with that calculated on the assumption that the interaction of chloroamine and hydrochloric acid is the slow stage whilst no agreement is found with the value calculated on the alternative assumption that the interaction between acetanilide and chlorine is the slower.

§ 3. Experimental.

The measurement of the speeds of chloroamine formation depends on the fact demonstrated by Orton and Jones (*loc.* cit.) that chloroamine formation and nuclear chlorination are simultaneous side reactions,

$$Cl_2 + \text{anilide} \rightleftarrows \begin{matrix}\text{chloroamine} + HCl \\ \text{chloroanilide} + HCl\end{matrix}$$

[1] Soper: J. Chem. Soc., **127**, (1925).

[2] Jakowkin: Z. physik. Chem., **29**, 813 (1898).

The ratio of chloroamine to chloroanilide formed gives the ratio of the respective velocity coefficients. The speeds of nuclear chlorination were themselves measured in the presence of sufficient $H^{\cdot}$ and Cl' ions to prevent appreciable formation of the chloroamine. The fall of iodine titre of a mixture of anilide and chlorine then gives a measure of the rate at which chlorine is disappearing from the system to form C-chlorinated derivatives.

Measurement of the speeds of nuclear chlorination. The source of chlorine was a mixture of Chloramine-T and hydrochloric acid, $C_7H_7SO(ONa)$: $NCl + {}_2HCl \rightleftarrows C_7H_7SO_2NH_2 + NaCl + Cl_2$. In the presence of the excess of hydrochloric acid necessary to prevent *N*-chlorination of the anilide, the equilibrium between Chloramine-T and hydrochloric acid is displaced with production of 100% chlorine. This source of chlorine was used in preference to chlorine water owing to its greater stability and convenience in handling. The stability of chlorine in the presence of Chloramine-T and of *p*-toluene-sulphonamide was shown by examination of the titre of a mixture of Chloramine-T and *M* hydrochloric acid contained in a flask stoppered with a ground-in pipette and fitted with a side arm connected to a washbottle containing the same mixture. Removal of a quantity of the solution for analysis caused the entry of a gaseous mixture into the bottle which was identical with that already present. If this precaution is omitted there is readjustment of the chlorine between the phases and consequent fall of the chlorine concentration in the liquid phase. Even under the conditions outlined a slight disappearance of chlorine was experienced but is negligible in comparison with that occurring in the presence of the anilides examined. It was found, by aspirating air over the surface of the liquid mixture, that the rate of escape of chlorine when an anilide is present was also negligible except when the solution was agitated.

Mixtures of Chloramine-T, hydrochloric acid and the anilide were made up at 25.0°, the Chloramine-T solution being added last to start the reaction. Portions of the mixture were withdrawn by a pipette at suitable time intervals, run into oxygen-free potassium iodide solution and the liberated iodine titrated against thiosulphate. The necessary concentration of hydrochloric acid required to cause the full production of chlorine from Chloramine-T was found to be from 3 to 4 molal, since further increase in concentration did not increase the speed of chlorination but actually caused a slight decrease, probably due to some slight removal of free chlorine as hydrogen tri-chloride. In the case of acetanilide portions were withdrawn every 10 secs., introducing an unavoidably large timing error. Its effect on the velocity coefficient is estimated at about 10-15%. The results obtained are given in Table II.

Measurement of the relative rates of chloroamine formation and of nuclear chlorination.—The method adopted was to add the requisite amount of hypochlorous acid to a mixture of excess of the anilide and 0.1M hydrochloric acid. The hydrochloric and hypochlorous acids form chlorine and since the chlorine is formed *in situ* it is surrounded by excess of the anilide, thus allowing the simultaneous side reactions to proceed unmasked by consecutive reactions which might be caused by local excess of chlorine. The iodine titre of the

mixture was measured at suitable time intervals and was found to fall quickly to a practically constant value. The fall of titre represents the nuclear chlorination, whilst the residual titre represents the chloroamine formed. The concentration of hydrochloric acid which is necessarily present to prevent hydrolysis of the chlorine has no appreciable effect on the amount of chloroamine formed, since the rate of interaction of these chloroamines with M/10 hydrochloric acid is negligible compared with their rates of formation. The results obtained are given in Table III and lead to the velocity coefficients of chloroamine formation given in Table II.

TABLE III

Relative speeds of *N*- and *C*-chlorination of anilides at 25.0°

	C_6H_5NHAc	$C_6H_4\begin{matrix}NHAc\\Cl(2)\end{matrix}$	$C_6H_4{}^{NHAc}_{Cl(4)}$	
Initial titre of 10 c.cs.	100.0	10.00	10.00	c.cs.
Final titre of 10 c.cs.	0.75	9.31	4.75	c.cs.
[chloroamine] / [chloroanilide] formed	0.0076	13.2	0.905	

The necessity of the presence of a large excess of the anilide is well exemplified in the case of acetanilide. When the chlorine and the anilide are equimolar, a considerable fraction of the chlorine reacts with the chloroanilides to form chloroamines which appear in the final titre. The ratio of chloroamine to chloroanilide formed becomes constant in the presence of an 8-fold excess of the anilide. The results are given in Table IV.

TABLE IV

[acetanilide]/[chlorine]	1	2	4	8	12
[chloroamine]/[chloroanilide]	0.064	0.010	0.008	0.00756	0.00768

Of the chloroamine formed when chlorine and acetanilide interact in eqimolar proportions only 12% is acetylchloroaminobenzene, the remainder being composed of the chloroamines of the chloroanilides.

Measurement of the rate of interaction of hydrochloric acid and acetylchloroaminobenzene.—The chloroamine was prepared by the method of Chattaway and Orton[1] and was dissolved in water redistilled from acid permanganate solution. The phenol and *p*-cresol used were redistilled Kahlbaum preparations, were quite colourless and when mixed with the chloroamine solution caused no detectable fall in the iodine titre in 7 hours at 25°.

In conclusion, I wish to thank Professor K. J. P. Orton, F. R. S., for suggesting this work and for helpful criticism.

University College of North Wales,
Bangor.
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[1] J. Chem. Soc., **73**, 1046 (1899).

L 2-42

ADSORPTION FROM SOLUTION BY ASH-FREE ADSORBENT CHARCOAL. III

A Comparison of Results obtained with Ash-free and Impure Charcoal*

BY ELROY J. MILLER

The various studies on adsorption from solution by pure ash-free charcoals have yielded results that have been consistently reproducible and concordant and at the same time so at variance with many of the data reported in the literature on adsorbent charcoals that it seems desirable to recapitulate briefly the results so far obtained and point out the causes of the discrepancies and their bearing on the more important conclusions arrived at from data obtained with the impure charcoals.

Perhaps the simplest method of dealing with the subject is to summarize briefly the more important findings with the ash-free charcoals and then compare them with the results obtained under comparable conditions with the impure charcoals and finally present additional data with both pure and impure materials in support of the conclusions presented.

Results with Activated Ash-Free Sugar Charcoal

Adsorption of Basic and Acid Dyes. Basic and acid dyes of the electrolyte type had frequently been chosen for use in adsorption studies with charcoals with the view of determining whether or not the reaction of the solutions could be changed through adsorption by a neutral inert adsorbent. It was evident at the outset that pure charcoal does adsorb these substances hydrolytically.[1] Under certain definite conditions the basic dyes such as methylene blue and crystal violet were completely adsorbed and their solutions left neutral. Under others the solutions after adsorption were strongly acid. With acid dyes such as sodium and ammonium eosins and sodium and ammonium picrates quite the reverse was true. Solutions of these salts after adsorption were strongly alkaline. These changes in reaction had been expected because, as a general rule, organic substances are adsorbed more than the inorganic ones by charcoal. With the organic dyestuff radicle in one case the anion and in the other the cation these highly adsorbed dyes should present ideal conditions for selective adsorption involving hydrolytic splitting by charcoal. When the changes in reaction were observed it seemed reasonably certain that hydrolytic adsorption by the charcoal was responsible for the changes in reaction since the charcoal was free from either alkaline or acidic impurities. Other experiments pointed to the same conclusion.[2] It was desirable, however, to see whether hydrolytic adsorption could be demonstrated with solutions of simple neutral salts.

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[1] Bartell and Miller: J. Am. Chem. Soc., **44**, 1866 (1922); **45**, 1106 (1923).

[2] For the sake of brevity and clarity only the salient facts and experiments will be dealt with in this paper. For details of experimental procedure and discussions the original papers should be consulted.

Hydrolytic Adsorption of Neutral Salts. A few tests with pure activated sugar charcoal and solutions of neutral salts indicated that there, too, hydrolytic adsorption was demonstrable. Solutions of salts of bases such as sodium, potassium, ammonium, barium, calcium, and magnesium became more alkaline after treatment with pure charcoal while solutions of salts of less basic and noble metals such as aluminum, iron, mercury, silver, gold, and platinum changed little or became more acid. Salts of the noble metals, silver, gold and platinum were reduced to metallic form. From these results it became evident that the pure charcoal adsorbed preferentially the acid and set free alkali from salts in aqueous solutions. An investigation of the adsorbability of a number of acids and bases gave further evidence of this fact.[1]

Adsorption of Acids and Non-Adsorption of Bases by Activated Sugar Charcoal. Adsorption data on a number of bases and acids of representative types revealed striking regularities. Three facts were outstanding. The first was that the hydroxides of sodium, potassium, ammonium, barium, calcium, and magnesium were not adsorbed at all by pure activated sugar charcoal. The second point of importance was the marked difference in adsorbability of the various types of acids. Acids of the aromatic type such as benzoic and salicylic were the most strongly adsorbed. Dicarboxylic acids such as succinic and malic were adsorbed more than the lower members of the aliphatic series, formic, acetic, and propionic. The inorganic acids, hydrochloric, nitric, sulfuric, hydrobromic, and perchloric were the least adsorbed. The third point was that the introduction of hydroxyl and amino groups into organic acids of the various types invariably resulted in a decreased adsorption. Thus, o-hydroxybenzoic acid (salicylic acid) and o-aminobenzoic acid (anthranilic acid) were adsorbed less than benzoic acid. Hydroxysuccinic acid (malic acid) was less adsorbed than succinic acid and dihydroxysuccinic acid (tartaric acid) was in turn less adsorbed than malic acid while aminosuccinic acid (aspartic acid) was very much less adsorbed. Hydroxypropionic acid (lactic acid) was less adsorbed than propionic acid while aminoacetic acid (glycocoll) was not adsorbed at all. The effect of the amino group was much greater than that of the hydroxyl group.

The fact that the sugar charcoal adsorbed acids but did not adsorb bases was in harmony with the fact that the salt solutions mentioned above became alkaline after treatment with the charcoal and strengthened the conviction that hydrolysis was involved in adsorption from these solutions. Complete and incontrovertible proof of hydrolytic adsorption, however, became possible when methods were developed for the quantitative removal of adsorbed acids from charcoal.[2]

Quantitative Removal of Adsorbed Acids from Charcoal: If the alkali, liberated in adsorption from salt solutions is due to hydrolytic adsorption, then it necessarily follows that an equivalent amount of acid must be adsorbed on the charcoal. Methods were sought whereby the amounts of the adsorbed

[1] Bartell and Miller: J. Am. Chem. Soc., **45**, 1106 (1923).
[2] Miller: J. Am. Chem. Soc., **46**, 1150 (1924).

acids might be estimated. It was soon found that several methods could be used satisfactorily with the sugar charcoal. One method based on the well known fact that substances are less adsorbed from organic solvents than from water was most satisfactory for use with organic acids; the other method based on the fact that sugar charcoal did not adsorb the hydroxides was found most suitable with inorganic acids. The adsorbed organic acids could conveniently be removed from the charcoal and estimated by shaking a water suspension of the charcoal with an immiscible organic liquid such as benzene or nitrobenzene and titrating the acid in the water phase with the aid of suitable indicators. The adsorbed inorganic acids could be determined more readily by boiling the charcoal several times with a given amount of standard alkali and titrating the alkali remaining in the filtrates and washings.

Trials with samples of activated sugar charcoal to which known amounts of acids of various types had been added showed that acids such as benzoic, salicylic, succinic, oxalic, acetic, hydrochloric, sulphuric, and nitric could be removed and quantitatively estimated by these methods. The next step, of course, was to treat solutions of salts with the charcoal, determine the amount of alkali set free, and examine the charcoal for adsorbed acid.

Complete Proof of Hydrolytic Adsorption. An examination of the charcoals after treatment with salt solutions showed that, in all cases where the solutions became more alkaline after adsorption, there existed on the charcoal a quantity of acid exactly equivalent to the amount of base set free. In the cases of salts such as the chlorides and sulphates of sodium or potassium it was found that the amount of chloride or sulphate removed from the charcoal was equivalent to the amount of acid removed from the charcoal. Here, then, was complete proof of hydrolytic adsorption. The method of preparation of the charcoal precluded the possibility of attributing the effects to impurities in the adsorbent. The base set free in the solution was equivalent to the acid recovered from the charcoal after adsorption. The acid recovered was the same as that from which the original salt had been derived.

Adsorption from Solutions of Acid-Salt and Alkali-Salt Mixtures. With the proof of hydrolytic adsorption established, it became of interest to study the behavior of the charcoal in solutions of mixtures of salts and acids and of salts and bases as had been done with impure charcoals by other investigators.

It was soon found[1] that pure sugar charcoal, in keeping with its property of adsorbing acids but not bases, adsorbed more acid from a mixture of sodium chloride and hydrochloric acid than from a solution of hydrochloric acid alone but on the other hand did not adsorb any alkali from a mixture of sodium hydroxide and sodium chloride. On the contrary, the charcoal was still able to adsorb sodium chloride hydrolytically in solutions of hundredth normal sodium hydroxide. Additional sodium hydroxide appeared in solution from the splitting of the sodium chloride. In the control experiments in which relatively large amounts of charcoal were used with hundredth normal alkali without any salt present it was observed that after adsorption the concentra-

[1] Miller: J. Am. Chem. Soc., **47**, 1270 (1925).

tion of alkali was somewhat greater than hundredth normal. Investigation showed, however, that the total amount of alkali had not changed and that the effect was due to negative adsorption.

Negative Adsorption of Bases: The negative adsorption of bases was determined for a number of concentrations of alkali varying from one two hundredth normal to tenth normal. It was found that the negative adsorption increased with increase in concentration of the alkali but not proportionally. The amount of water adsorbed decreased with increase in concentration of the alkali.

Positive and Negative Adsorption from Salt Solution. The fact that in the hydrolytic adsorption of salts of inorganic acids the anion of the salt appeared on the charcoal in an amount equivalent to the acid adsorbed indicated that the adsorption was exclusively hydrolytic. That is, there was apparently no adsorption of the salt as such. Further evidence was sought on this point and on the question of whether or not this was true of adsorption from solutions of all salts. A study was made, therefore, of the adsorption of a series of potassium salts of organic and inorganic acids. The concentration of the potassium in solution before and after adsorption as well as the amount of alkali appearing after adsorption was carefully determined. The results indicated clearly that adsorption from solutions of the inorganic salts was entirely hydrolytic while that of the salts of the highly adsorbed acids such as benzoic and salicylic was partly hydrolytic and partly molecular. The concentration of potassium in solution after adsorption from solutions of the inorganic salts was greater than before, indicating that negative adsorption of the base took place and that some water was adsorbed along with the acid arising from hydrolysis of the salt. On the other hand, the concentration of the potassium after adsorption from solutions of potassium benzoate and salicylate was less than before adsorption. These salts were, therefore, partly hydrolytically and partly molecularly adsorbed.

Difficulty of removing Adsorbed Acids from Charcoal by washing with Water. The knowledge of the behavior of activated sugar charcoal toward acids and bases, together with the previously mentioned methods of determining the quantity of adsorbed acid on charcoals, afforded a means of throwing light on the efficacy of the usual method of prolonged washing with water to remove acids with which charcoals had been treated in attempts at purification. Hydrochloric acid was used in an investigation of this question.[1] The charcoal adsorbed quantitatively a given amount of the acid at room temperature, leaving the suspension strictly neutral. Repeated washing at room temperature did not remove the slighest trace of acid. When suspended in conductivity water and filtered at boiling temperature a small amount of acid was removed. Fifteen such treatments, in which the boiling was continued for various periods up to eight hours before filtering, removed only half of the adsorbed acid. The later extractions removed only minute traces of acid. But determination of the amount of acid remaining on the charcoal

[1] Miller: J. Am. Chem. Soc., 47, 1270 (1925). See also Michigan Experiment Station Technical Bulletin, No. 73, page 52.

by one of the methods previously mentioned, supported by chloride determination, showed that only half of the acid had been removed by the prolonged boiling with water. It was evident that continued extraction with boiling water would not remove all the adsorbed hydrochloric acid. This experiment clearly indicates that the usual method of "purifying" charcoals, by extracting with hot hydrochloric acid and then washing with boiling water until chlorine could no longer be detected in the filtrate, left adsorbed acid on the charcoal.

Hydrochloric acid is one of the acids least adsorbed, and yet the amounts thus held by active charcoals are quite appreciable and sufficient to alter markedly the behavior of the charcoal. Much larger quantities of the more highly adsorbed acids such as benzoic acid were held in this fashion by the activated sugar charcoal.[1]

Adsorption and Interfacial Tension. It was pointed out[2] that the introduction of the hydroxyl and amino groups in organic acids resulted in decreased adsorption. This fact, together with that of the negative adsorption of bases[3] made it seem probable that the charcoal plays the same role in a charcoal-solution interfacial system that the organic liquid plays in organic liquid-aqueous solution systems and that the Langmuir-Harkins theory of the effect of polar groups applies to adsorption from solution by charcoal. Negative adsorption of the strong inorganic bases which raise the surface tension of water and the decreasing adsorption of succinic, malic, and tartaric acids in the order of their increasing effect on the raising of surface tension brought the action of charcoal in still closer analogy with the systems to which the Gibbs adsorption theorem applies.

Purification of Adsorbent Charcoals. That activated sugar charcoal did not possess unique properties characterizing it from all other active charcoals was proved when a method for the purification of commercial charcoals[4] made it possible to remove impurities from the types of charcoals used by previous investigators in adsorption studies. Investigation of adsorption by charcoals of animal, vegetable, and carbohydrate origin showed that these charcoals, when freed from inorganic matter and other impurities, all possessed the same properties which were identical with those of pure activated sugar charcoal.[5] These facts, together with experiments in which many of the anomalous results reported in the literature could be reproduced and explained by treatment of activated sugar charcoal or the purified ash-free charcoal with appropriate substances, make it certain that many of the supposedly characteristic properties attributed to charcoals prepared from various materials were in reality due to the inorganic matter, adsorbed acids, and other impurities in the charcoal.

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[1] Unpublished data.
[2] Bartell and Miller: J. Phys. Chem., **28**, 992 (1924).
[3] Miller: J. Am. Chem. Soc., **47**, 1270 (1925).
[4] Miller: J. Phys. Chem., **30**, 1031 (1926).
[5] Miller: J. Phys. Chem., **30**, 1162 (1926).

All active, ash- and acid-free charcoals, from whatever carbonaceous source prepared, have the same property of adsorbing acids but not bases. They adsorb certain salts exclusively hydrolytically and certain others partly hydrolytically and partly molecularly. These properties will vary only in magnitude depending on the extent to which the carbon has been activated. It is useless to compare the activity of such charcoals as blood, animal, wood, and sugar charcoals as has been done in the past, for the activity is not a characteristic property of charcoal from any given source. Charcoals of an equally high order of activity can be prepared from all of these sources.

Results with Impure Charcoals

Adsorption of Acid and Basic Dyes. In general, the behavior of the impure charcoal is quite different from that of the ash-free charcoals. An inspection of the data in the literature reveals many contradictory findings, particularly with regard to adsorption from salt solutions. The question of the existence of hydrolytic adsorption by charcoal had been frequently attacked. With simple inorganic salts the results were so inconsistent that they were not very generally accepted. The use of acid and basic dyes of the electrolyte type, because of the great difference in adsorbability of the cation and anion, was thought to offer possibilities for the solution of the question. Freundlich and Losev[1] using crystal violet, a basic dye, found that the organic cation was adsorbed but the chloride anion was left quantitatively in solution. The solution remaining after adsorption was acid. Subsequently Freundlich and Neumann[2] found that the acid in solution after adsorption of this dye accounted for only a small fraction of the total chloride and the chloride, therefore, was largely in the form of a salt and not hydrochloric acid. Michaelis and Rona[3] in 1919 found, on the contrary, that both acid and basic dyes were molecularly adsorbed although ionic exchange with impurities in the charcoal was also a factor in the adsorption. The solutions after adsorption of these dyes were neutral.

Adsorption of Salts. A detailed account of the results of studies of adsorption from salt solutions by charcoal is given elsewhere[4] and it is unnecessary to do more than point out a few of the more recent instances to illustrate the contradictory nature of the results as far as hydrolytic adsorption is concerned. Lachs and Michaelis[5] in 1911 in a study of adsorption of neutral salts obtained evidence indicating that potassium chloride was hydrolytically adsorbed. The decrease of the chlorine content was easily detected as was the non-adsorption of the potassium but the presence of potassium hydroxide in the solution after adsorption could not be demonstrated with certainty. In 1919 Rona and Michaelis[6] again took up a study of the adsorption of electrolytes

[1] Z. physik. Chem., **59**, 284 (1907).
[2] Z. physik. Chem., **67**, 538 (1909).
[3] Biochem. Z., **97**, 57 (1919).
[4] Bancroft: "Applied Colloid Chemistry", 138 (1926); J. Phys. Chem., **24**, 342 (1920)
[5] Kolloid-Z., **9**, 275 (1911).
[6] Rona and Michaelis: Biochem. Z., **94**, 240 (1919).

from solution. From this work and from their work with acid and basic dyes mentioned above they concluded that hydrolytic adsorption by charcoal did not take place. Odén and Andersson[1] several years later came to the same conclusion and expressed the opinion that whenever a solution was acid or alkaline after adsorption the acidity or alkalinity was due to impurities displaced from the adsorbent. These conclusions were generally accepted and the theory of hydrolytic adsorption was practically abandoned.[2]

Adsorption of Acids and Bases. Toward acids and bases the impure charcoals exhibited a far more consistent behavior than was the case in adsorption from salt solutions. Acids as a rule were among the substances most strongly adsorbed.[3] The organic acids were strongly adsorbed while the inorganic ones were less strongly adsorbed. The increase in adsorption with ascent in the homologous series of aliphatic acids has been pointed out[4] as in keeping with surface tension effects (Traube's rule). It is worthy of mention that in the adsorption of acids the impure charcoals show the same selectivity as that exhibited by ash-free charcoals.

Reports on studies of adsorption[5] of electrolytes by charcoals invariably stated that the inorganic bases such as sodium and potassium hydroxides were positively adsorbed. The magnitude of the adsorption usually was of an order somewhat lower than that of the inorganic acids.

Prior to the discovery that activated ash-free sugar charcoal does not adsorb bases there was nothing to suggest that the removal of alkali from solution by the ordinary charcoals differed in any way from the adsorption of acids. Subsequent investigation into the causes of the difference in behavior of the charcoals showed that the removal of the bases was not a true adsorption. An understanding of the causes of the apparent adsorption of bases by charcoal opened the way for a clear explanation of the contradictory reports in the literature on adsorption from solution by charcoal. It seems worth while to discuss in some detail these reasons for the various discrepancies as they have been deduced from the experimental results with pure charcoal.

Causes of Anomalous Results

Causes of Apparent Adsorption of Bases. It has been pointed out in connection with the work on pure charcoal that unless certain precautions are taken an apparent adsorption of bases would be observed. This apparent adsorption may be due to a number of causes. First, if the pure charcoal, before addition to a solution of a base, has been treated with acid the adsorbed acid will of course neutralize some of the alkali. If the adsorbed acid is an inorganic one the effect will be exclusively a replacement of part of the hydrox-

[1] J. Phys. Chem., **25**, 311 (1921).

[2] Freundlich: "Kapillarchemie", 276 (1923).

[3] Freundlich: Z. physik. Chem., **57**, 385 (1907).

[4] Freundlich: "Kapillarchemie", 264 (1923).

[5] Lachs and Michaelis: Kolloid-Z., **9**, 275 (1911); Estrup, Kolloid-Z., **14**, 8 (1914); Lachs, Z. physik. Chem., **91**, 155 (1916); Rona and Michaelis, Biochem. Z., **94**, 240 (1919); **97**, 85 (1919); Schilow and Lepin, Z. physik. Chem., **94**, 25 (1920); Yajnik and Rana, J. Phys. Chem., **28**, 267 (1924).

ide in solution by salt since salts of inorganic acids are not molecularly adsorbed. If the adsorbed acid is an highly adsorbed organic acid part of the hydroxide will be neutralized and held adsorbed by the charcoal as the salt of that acid since salts of highly adsorbed acids are partly molecularly adsorbed. In either case titration of the alkaline solution after treatment with the acid-bearing charcoal would show a loss of alkalinity. A determination of the concentration of the cation, however, would show no decrease in the case of the inorganic acid but would show a loss in the case of the organic one. The presence of adsorbed acid on charcoals has undoubtedly been the factor responsible for most of the reports in the literature that bases are adsorbed. The difficulty with which the last traces of adsorbed acids are removed from charcoal has been pointed out above in connection with the experiment on the quantitative removal of hydrochloric acid from pure sugar charcoal. An examination of the literature on adsorption from solution reveals the fact that most of the charcoals used in these studies had been treated with acids in attempts at purification. It is not surprising that the adsorbed acids were not detected in the earlier work. It need only be recalled that the work with the ash-free charcoals showed that the reaction of a water suspension of charcoal is no criterion of the presence or absence of acid on the charcoal. A suspension of charcoal in water may even have an alkaline reaction and yet the charcoal carry adsorbed acid. This necessarily follows from the fact that charcoal hydrolytically adsorbs acid from a neutral salt and leaves the base in solution. (Methods whereby the presence or absence of adsorbed acid on charcoal may be detected have been described in a previous paper.[1])

A second manner in which bases may appear to be adsorbed is by reaction with adsorbed salts of the type of the basic dyes, It was shown in the early work[2] that when a pure charcoal carrying adsorbed methylene blue is treated with sodium hydroxide there is an exchange of the chloride ion of the adsorbed methylene blue with the hydroxyl ion of the sodium hydroxide. Sodium chloride remains in solution and the insoluble methylene blue hydroxide remains on the charcoal. Thus the possibility of ionic exchange or metathesis with adsorbed impurities in which an insoluble hydroxide may be formed must be kept in mind as a possible reason for the apparent adsorption of bases.

Still a third way in which it may appear that the bases are adsorbed is through failure to recognize the effect of carbon dioxide on the alkalies. In many of the adsorption studies the alkalies were used in solutions as dilute as fiftieth and hundredth normal and the titrations were made with methyl orange as indicator. It has since been pointed out[3] that methyl orange is not a sensitive indicator and should not be used for solutions less than fifth-normal. Experience with the pure charcoals and dilute solutions of alkalies has been that large errors are introduced in titration unless sensitive indicators such as phenol red or bromothymol blue are used and precautions

[1] Miller: J. Phys. Chem., **30**, 1162 (1926).
[2] Bartell and Miller: J. Am. Chem. Soc., **44**, 1866 (1922).
[3] Sutton: "Volumetric Analysis", 11th Edition, page 36.

are taken to boil off carbon dioxide.[1] From the work with the pure charcoal it seems quite likely that failure to eliminate the effect of carbon dioxide has also been an important factor in many cases where positive adsorption of bases has been reported.

Causes of the Contradictory Reports on Hydrolytic Adsorption. In the course of the studies of hydrolytic adsorption by activated sugar charcoal attempts were made to determine whether by the addition of suitable substances to the pure charcoals the conflicting results reported in the literature on impure charcoal could be duplicated and explained. The expectation was, of course, that the anomalous results were due to adsorbed acids or alkaline impurities (ash). Pure charcoals were, therefore, treated with known amounts of acids or alkalies to simulate these conditions.

The presence of acid on the charcoal altered profoundly the behavior of the charcoal in its adsorption of basic dyes, acid dyes, and neutral salts. Much more acid was set free when the basic dyes were adsorbed by acid-bearing charcoals than when the charcoal carried no adsorbed acid. The hydrolytic adsorption in this case was magnified. On the other hand, the hydrolytic adsorption of the acid dyes and neutral salts was entirely obscured when a small amount of adsorbed acid was on the charcoal. The solutions after adsorption were neutral. With larger quantities of acid on the charcoal it was even possible, with certain salts, to displace some of the acid from the charcoal, thus leaving the solution acid instead of alkaline as in the case of these salts with pure acid-free charcoal.

Pure charcoals that had been treated with slightly soluble basic substances or suspended in dilute solutions of alkalies showed equally contradictory results. Solutions of the basic dyes after adsorption were left neutral or slightly alkaline depending upon the amount of dye adsorbed and the amount of base available. Solutions of the acid dyes and neutral salts after adsorption were more alkaline than when adsorbed by the untreated pure charcoal.

These examples are sufficiently indicative of the great variety of results that can be obtained in adsorption by pure charcoal that has been treated with acid or basic substances. It is obvious that the results would be highly confusing and contradictory if the previous treatment of the charcoal were not known. That this has been the situation in many or all of the adsorption studies reported in the literature is evident when the composition of the charcoals used in those studies is examined.

Experimental Verification of the Causes of Anomalous Results with Impure Charcoals

Charcoals used in Previous Work. The great majority of researches on adsorption from solution were carried out with blood charcoal for the reason that it possessed the highest adsorptive capacity of all the available charcoals. Sugar charcoal was used somewhat but usually for the purpose of pointing out its inactivity compared with that of blood charcoal. In comparatively

[1] Miller: J. Am. Chem. Soc., **46**, 1150 (1924); **47**, 1270 (1925).

recent years methods for the activation of charcoal have become generally known and activated charcoals prepared from wood and other vegetable sources have been used occasionally. Almost without exception the blood charcoal used in the researches was "Merck's Blood Charcoal, Purified by Acids." Nothing was known about the preparation of this product and there does not seem to be anything in the literature that throws any light on its history. Apparently it has been a fairly uniform product, at least as far as ash content is concerned for the past twenty years, for Freundlich and Losev[1] in 1907 reported an ash content of 7-8% and these values have been reported by numerous investigators since that time. Within the past year, however, a quantity of charcoal of this brand with entirely different characteristics has been received. Its adsorptive capacity is 40% greater than that of previous lots, its ash content 2.40% instead of 8%, and its nitrogen content 0.15% instead of the usual 0.6% in the previous lots that had been examined in recent years. Attempts at purification, reported in the literature, by treatment with concentrated acids were futile and for the most part the charcoal was used without any attempt at purification. The main point to be brought out is that little or nothing was known about the history of the preparation and treatment of the adsorbents used in the majority of investigations on adsorption from solution by charcoal. In view of this situation it was desirable, therefore, to examine the impure charcoals and test further the inferences drawn from the results with the pure sugar charcoal.

Effect of Heating on Properties of Charcoal. It was pointed out in an early paper[2] that these ash-bearing charcoals were always alkaline after they had been ignited. Subsequently,[3] it was shown that removal of the ash and heating at 1000° did not change the adsorptive capacity of these charcoals for acids but they no longer had any effect on solutions of the alkalies. This evidence supported the contention that adsorbed acids existed on the charcoals and were responsible for the apparent adsorption of bases. Further evidence on this point has been obtained by heating specimens of various lots of blood charcoal in silica tubes sealed at one end and collecting the acids driven off. With all the older lots, heating below a red heat drove off some hydrochloric acid. This probably represented adsorbed acid with which the charcoal had been treated in 'purifying by acids.' As the temperature was raised substances with strong oders of cyanogen compounds were driven off amd at still higher temperatures the gases were alkaline. This indicated quite clearly that there was present in the charcoal undecomposed organic nitrogenous matter, probably in the form of complex insoluble organic acids resulting from the incomplete decomposition of the dried blood.

The new samples of blood charcoal with the high activity, low ash, and low nitrogen content mentioned above behaved quite differently on heating. Copious quantities of sulfuric acid were given off, but no trace of chloride,

[1] Z. physik. Chem., 59, 284 (1907).
[2] Bartell and Miller: J. Am. Chem. Soc., 44, 1866 (1922).
[3] Miller: J. Phys. Chem., 30, 1162 (1926).

indicating that the charcoal had been treated with sulfuric acid. This charcoal neutralized large quantities of sodium hydroxide with the concomitant appearance of the sulfate in the solution.

Additional evidence supporting the hypothesis of adsorbed acids and undecomposed organic acids as the cause of the apparent adsorption of bases was obtained in three ways: (1) A sample of blood charcoal was heated and the acid gases given off were adsorbed in standard alkali. The hydrochloric acid caught in the alkaline solution represented only a fraction of the total amount of alkali neutralized. The remainder of the neutralization was due to organic acids, carbonic, hydrocyanic, etc. After the heating, the charcoal was alkaline and had lost its power of neutralizing sodium hydroxide. (2) Sugar was charred at a low temperature without activation. The char gave an acid reaction when suspended in water and took up, or neutralized, sodium hydroxide. It was then heated at 1000° after which it neither adsorbed acids nor had any effect on a solution of sodium hydroxide. The inactive charcoal when activated by heating in a limited supply of air adsorbed acids but not bases. (3) Purified blood charcoal which adsorbed acids but not bases was treated with alcoholic methyl red acid to determine whether a complex water-insoluble organic acid when adsorbed on the pure charcoal would give it the properties of taking up or neutralizing bases which it possessed before purification as the hypothesis demanded. The charcoal carrying the adsorbed methyl red acid was suspended in standard alkali and it was found that the capacity of the charcoal for taking up bases exceeded that of the original charcoal. When the charcoal carrying the adsorbed methyl red acid was ignited it again lost its power of taking up alkalies.

Since the data on these experiments have not been published, heretofore, the following results are presented. They are typical of the results obtained in the examination of numerous samples of charcoals of animal, vegetable, and carbohydrate origin.

The Effect of Various Treatments on the Action of Charcoals on Benzoic Acid and Sodium Hydroxide

1. Sugar charred below a Red Heat.
   cc N/50 sodium hydroxide neutralized per gram of char.....14.4
   cc N/50 benzoic acid adsorbed per gram of char..... 0.0
2. Sugar Char heated at 1075° in the Absence of Air.
   (Not activated.)
   cc N/50 sodium hydroxide neutralized per gram of charcoal..... 0.0
   cc N/50 benzoic acid adsorbed per gram of charcoal..... 0.0
3. Sugar Charcoal activated at 1075°.
   cc N/50 sodium hydroxide neutralized per gram of charcoal..... 0.0
   cc N/50 benzoic acid adsorbed per gram of charcoal.....228.0
4. Blood Charcoal (as received).
   cc N/50 sodium hydroxide neutralized per gram of charcoal..... 19.0
   cc N/50 benzoic acid adsorbed per gram of charcoal.....193.1

5. Blood Charcoal (purified) Inorganic Matter removed and heated at 1075°.
cc N/50 sodium hydroxide neutralized per gram of charcoal..... 0.0
cc N/50 benzoic acid adsorbed per gram of charcoal.....208.8
6. Purified Blood Charcoal carrying Adsorbed Methyl Red Acid.
cc N/50 sodium hydroxide neutralized per gram of charcoal..... 24.4
cc N/50 benzoic acid adsorbed per gram of charcoal.....191.4
7. Purified Blood Charcoal carrying Adsorbed Methyl Red Acid. Ignited at 1075° to Destroy Methyl Red Acid.
cc N/50 sodium hydroxide neutralized per gram of charcoal..... 0.0
cc N/50 benzoic acid adsorbed per gram of charcoal. 187.0

The results of these experiments force the conclusion that the apparent adsorption of bases by charcoals is due to the presence of adsorbed inorganic acids and complex organic material of an acid nature resulting from the incomplete decomposition of the substance from which the charcoals are prepared. Thus the inference, based on non-adsorption of alkalies by pure sugar charcoal, that the so-called adsorption of bases by ordinary charcoals is not a true adsorption but only an apparent one and that it is due to the interaction and neutralization by acid impurities in the charcoal, seems fully verified.

Accordingly, it can readily be seen that each individually prepared lot of charcoal will have its own properties depending upon such factors as amount of ash, the extent of activation, the temperature to which it has been heated, and the thoroughness with which acids used in "purifying" have been removed. In the light of these facts the anomalous and contradictory results reported in the literature become intelligible and of greater value. The reasons are obvious why convincing proof of hydrolytic adsorption of salts and of the non-adsorption of bases was not forthcoming before pure activated charcoal was available.

Bearing of Results on Conclusions based on Previous Work with Impure Charcoals

Orders of Adsorbability of Salts. Numerous researches deal with the determination of the order of adsorbability of series of salts and of ions. Summaries of results of these researches are given by Bancroft,[1] Freundlich,[2] Svedberg,[3] and others and will, therefore, not be repeated here. It should be pointed out in connection with these researches that blood charcoal was used in all of them and it is, of course, obvious that the usual complicating factors were involved. Ionic exchange with the adsorbed acids and inorganic impurities undoubtedly took place and complicated matters. It was pointed out in a study[4] of adsorption from solutions of a number of potassium salts by pure activated sugar charcoal that hydrolytic adsorption is a factor that must be considered in determining the orders of adsorbability. It is necessary to

[1] Bancroft: "Applied Colloid Chemistry", 114 (1926).
[2] Freundlich: "Kapillarchemie", 287 (1923).
[3] Svedberg: "Colloid Chemistry", 177 (1924).
[4] Miller: J. Am. Chem. Soc., 47, 1270 (1925).

determine the change in concentration of both ions of a salt remaining in solution after adsorption. In the case of the simple inorganic salts, for example, the adsorption is entirely hydrolytic. Analysis showed that the concentration of the positive ion not only does not decrease but actually increases while the concentration of the negative ion decreases showing that there is no molecular adsorption of these salts but only adsorption of the acid and liberation of the base. It is obvious that the contradictory reports of the postive and negative adsorption of some of the simple inorganic salts can be accounted for by and were probably due to the analysis of the solution for only one or the other of the ions of the salt and to the presence in the charcoal of adsorbed acids and inorganic matter. In some orders of adsorbability potassium hydroxide appears first. In the light of the results with ash-free charcoals it should be last for it is negatively adsorbed.

Orders of Adsorbability of Ions. Discrepancies in the reports on orders of adsorbability of ions similar to those appearing for salts are found. They are undoubtedly due to the same causes discussed in the preceding paragraph for salts. The adsorbability of hydrogen and hydroxyl ions is of special importance since these ions have long been attributed with characteristic properties. Hardy[1] was the first to put forth the idea that hydrogen and hydroxyl ions possess certain characteristic properties by virtue of which they play a special role in the field of colloid chemistry. Perrin[2] later suggested that because of their abnormal mobility these ions were readily adsorbed and imparted to the adsorbent the charge which they carry. Because the hydroxides seemed to be adsorbed more than their salts the hydroxyl ion was placed first in the order of adsorbability of anions and because acids were adsorbed more than their salts the hydrogen ion was placed first in the order of adsorbability of cations.[3] Rona and Michaelis[4] tried to determine the relative adsorbability of hydrogen and hydroxyl ions by measuring the increase in adsorption of acids and bases caused by the addition of the neutral salts. They concluded that the adsorbability of these ions was of about the same order of magnitude. These conclusions served to strengthen the idea that hydrogen and hydroxyl ions possess similar and unique properties of adsorbability and by virtue of these play a special role in colloid chemistry.

When this work was repeated with pure charcoal, however, it was found as stated earlier in this paper that the adsorption of acids was increased by the presence of salts but no alkali was adsorbed from the alkali-salt mixtures. Provided this method of determining the relative adsorbability of the two ions is a valid one it is obvious that there is no adsorption of the hydroxyl ion while the hydrogen ion is highly adsorbed. In the order of adsorbability of cations the hydrogen ion should be among the highest while the hydroxyl ion should be at the end of the series of anions.

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[1] J. Physiol., **29**, 29 (1903).
[2] J. Chim. phys., **2**, 601 (1904).
[3] Michaelis and Rona: Biochem. Z., **94**, 240 (1919).
[4] Biochem. Z., **97**, 85 (1919).

There are other grounds for expecting hydrogen ions and hydroxyl ions to have unlike properties. The fact that the hydrogen ion is the positive electron or proton should lead one to expect it to exhibit inherently characteristic electrical properties and by reason of this fact per se it would be unreasonable to expect the hydroxyl ion to have equal and similar properties. These electrical effects in adsorption phenomena should overshadow in importance those of mobility to which Perrin attributed the unusual effects of these ions in colloid systems. But even in the matter of mobility an examination of the facts of adsorption shows that in general substances with anions of lower mobility are adsorbed most while those with anions of higher mobilities are adsorbed least. Accordingly, if the mobilities are causal factors and not merely concomitant, then it should follow that the hydroxyl ion should be least adsorbed since it possesses the highest mobility of all the anions. This is in harmony with the fact that potassium hydroxide with its fast moving hydroxyl anion is negatively adsorbed while potassium benzoate with its slow-moving benzoate anion is positively adsorbed. The same line of reasoning applied to cations would lead to the conclusion that the hydrogen ion is least adsorbed because it is the fastest cation. But from the fact that an acid is adsorbed more than its salts the hydrogen ion is first in the order of adsorbability of cations (excluding some organic cations). Thus both adsorption measurements and consideration of mobility of anions place the hydroxyl ion last in the order of adsorbability of anions. But, the mobility considerations do not support the position of the hydrogen ion as determined by the adsorption measurements. There is, however, not as close a correlation of mobility of cations with adsorption as in the case of the anions and it is entirely possible that the mobilities have nothing to do with the adsorbability of ions and are merely concomitant with the real factors determining adsorbability. Whatever the relative adsorbability of hydrogen and hydroxyl ions may be in other colloid systems the data on adsorption from solutions of acids, bases, and salts by pure charcoal show conclusively that their properties are radically different in charcoal-solution systems.

That the hydroxyl group does have special and characteristic properties of its own is apparent from other considerations. Langmuir[1] points out the fact that the hydroxyl group does not have any effect on the surface energy of a series of normal saturated aliphatic alcohols. They all have the same surface energy. This effect is explainable on the basis of the energy of the field surrounding the hydroxyl group. The hydrocarbon radicals are arranged in the surface so that the CH_3 groups form the surface while the hydroxyl group is turned toward the bulk of the solution. This is in effect a negative adsorption of that part of the molecule. It was pointed out above that the introduction of the hydroxyl radical into acids invariably cut down the adsorption of those acids by pure charcoal.

It seems, therefore, not merely accidental that the effect of the introduction of the hydroxyl group in organic acids is a decreased adsorption and

[1] "Colloid Symposium Monograph", 3, 50 (1925).

that the inorganic hydroxides are negatively adsorbed by pure charcoal. The underlying reason is to be sought for in the energy relationships involved in interfacial tension.

Summary

The more important results obtained in studies on adsorption from solution by activated sugar charcoal and purified ash-free adsorbent charcoal have been summarized and the following points discussed:

1. Proof of hydrolytic adsorption by active charcoal.
2. Non-adsorption of inorganic bases by active charcoal.
3. Negative adsorption of inorganic bases by active charcoal.
4. Positive and negative adsorption from salt solutions.
5. The applicability of the Langmiur-Harkins theory of the effect of polar groups to adsorption by charcoal.
6. All adsorbent charcoals when freed from organic and inorganic impurities and adsorbed acids have the same properties of adsorption from solution, viz. hydrolytic adsorption of salts, positive adsorption of acids, and negative adsorption of inorganic bases.
7. The causes of the contradictory reports on hydrolytic adsorption of salts, positive and negative adsorption of salts, and positive adsorption of bases by impure charcoal.
8. The significance of the results for the determination of orders of adsorbability of salts and of ions, particularly hydrogen and hydroxyl ions.
9. Additional data have been presented in support of the contention that the supposed adsorption of bases by unpurified charcoals is due to reaction with acid impurities in the charcoal.

East Lansing, Michigan.

THE DECOMPOSITION OF HYDROGEN SULPHIDE

BY H. AUSTIN TAYLOR AND CHARLES F. PICKETT[1]

The interest attached to the study of gaseous reactions and the elucidation of their mechanisms together with the present effort towards the discovery of purely unimolecular reactions suggested that the decomposition of hydrogen sulphide into hydrogen and sulphur might furnish such a reaction. The temperature at which such a reaction would proceed with measurable speed would necessitate the use of a quartz reaction system and even then the surface action might not be negligible. A preliminary investigation therefore was made of the reaction as it occurs on the surface of a hot filament, this being a convenient way of producing, locally, a high temperature.

The study of catalytic poisons points definitely to the inhibition which is brought about by sulphur compounds in general, and by hydrogen sulphide in particular. Maxted[2] has published a series of papers in which the inhibitory effects of several poisons, one of which is hydrogen sulphide, are discussed. It was shown that the adsorbing power of the platinum metals for hydrogen was greatly inhibited by hydrogen sulphide. When a small amount of this gas was allowed to enter the reaction chamber, the amount of hydrogen adsorbed was very small. However, when the chamber was heated to 100°C and evacuated, a volume of hydrogen equal to that of the hydrogen sulphide first introduced, was obtained, but no hydrogen sulphide came off. If now the catalyst was again tested for its adsorptive power, it adsorbed some hydrogen though not as much as it did before being poisoned. The sulphur remaining obviously exerts also a poisoning effect.

Such facts immediately suggest that the adsorption of hydrogen sulphide by platinum is extremely high and that this metal therefore at a high temperature ought to be an efficient catalyst for its decomposition since the hydrogen formed will not be adsorbed in the presence of excess hydrogen sulphide: the sulphur alone possibly causing complications. The study of the reaction made has brought out this point quite clearly and furnishes too an interesting case of gaseous inhibition.

Experimental

The method adopted for the study consists, in outline, of passing hydrogen sulphide at known rates of flow over a platinum filament, heated electrically to a known temperature, the effluent gases being analysed to evaluate the extent of decomposition.

Hydrogen sulphide of 99.5 per cent purity can be readily prepared from calcium sulphide as recommended by Pollitzer[3]. Kahlbaum's chemically

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[1] Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University.

[2] J. Chem. Soc., **115**, 1050 (1919); **117**, 1280(1920); **119**, 225, (1921).

[3] Pollitzer: Z. anorg. Chem., **64**, 121 (1909).

pure calcium sulphide in lump form was used in an ordinary Kipp generator with a solution of hydrochloric acid, made by mixing equal parts of concentrated acid and distilled water. Before connecting the generator to the remainder of the apparatus about four liters of H_2S were drawn off to ensure the complete removal of air. The gas was first dried by passing over calcium chloride, and finally dried before entering the reaction chamber by passing over phosphorus pentoxide. The gas after passage through the reaction chamber was absorbed in an almost saturated solution of potassium hydroxide.

The rate of flow of the gas was controlled by a flow-meter necessitating a very steady pressure. For this purpose, two Kipp generators connected in parallel were connected to the generator and used as a gasometer. A three-way stopcock was used at the mouth of the gasometer so that it could be permanently connected with both the generator and the flow-meter. Since the gasometer contained water it also served to remove all traces of hydrogen chloride carried over from the generator.

The flow-meter was of the type described by Benton[1] for small rates of flow. The capillary was about one centimeter in length blown in Pyrex glass. Distilled water was used in the manometer and was of course saturated with hydrogen sulphide.

The reaction chamber was similar in construction to that used by Hinshelwood.[2] The chamber was blown of Pyrex glass about eleven centimeters long and three centimeters in diameter. A fine platinum wire about ten centimeters long was stretched axially across the tube, connections to the wire being made by mercury contacts through inner seals. The inlet and outlet for the gas was effected by sealing two pieces of glass tubing, one at each end and on opposite sides of the tube. The two tubes for the mercury contacts, as well as the inlet and outlet tubes were bent vertically, so that the reaction chamber could be immersed in melting ice, the ends of the tubes being above water. The end of the outlet tube was fitted with a ground-glass joint bent in a horizontal position to accommodate the absorption bulb. Before the outlet tube was completed a small wad of cotton wool was placed in the tube to prevent any sulpher from being carried over. It was found from preliminary experiments that solid sulphur in the form of a smoke was carried over with the effluent gases when the cotton wool was absent.

The absorption bulb was of special construction to meet the demands of the experiment. No absorption apparatus which allowed bubbling could be used since it would seriously affect the readings of the manometer levels in the flow-meter. The bulb used therefore consisted of a tube seven centimeters long and one and a half centimeters in diameter. At one end a small piece of tubing was sealed vertically then bent in a horizontal direction and furnished with a ground joint to fit the reaction chamber exit. To the other end, a bulb of four centimeters diameter was attached by a short length of small tubing and terminating at its upper end with a ground joint of one centimeter diameter, to allow the bulb to be filled with pieces of solid potassium hydroxide.

[1] J. Ind. Eng. Chem., **11**, 623 (1919).
[2] J. Chem. Soc., **127**, 327 (1925).

The stopper of this ground joint was drawn off to a small tube to accommodate a small rubber cover during weighing, thereby preventing the absorption of carbon dioxide. This form of absorption bulb allows the tube to be partially filled with a nearly concentrated solution of potassium hydroxide, the bulb carrying pieces of the solid. The effluent gases then pass over the liquid where most of the H_2S is absorbed, the moist solid finally removing the last traces. The temperature of the filament was measured with a Hoskins optical pyrometer, a distinct image of the heated wire being obtained by using an

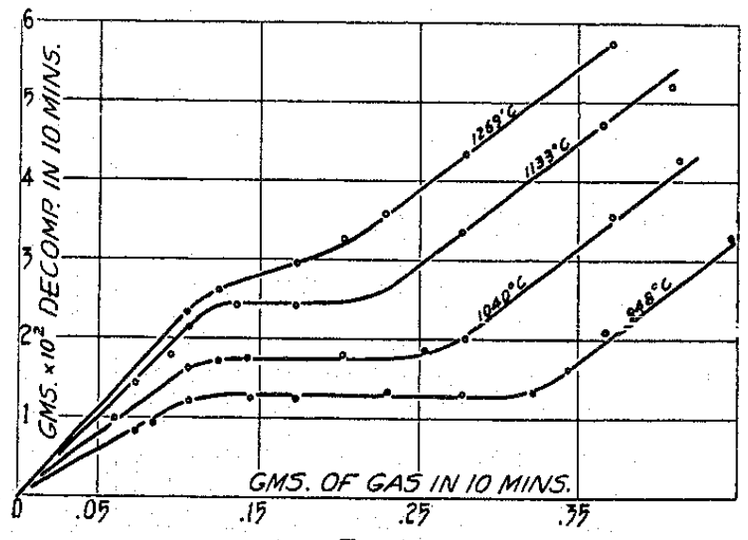


FIG. 1

auxiliary lens at the objective end of the telescope. The filament was maintained at constant temperature by manual operation of a rheostat in series with the platinum wire and two storage cells of six volts each. Any variation in the temperature would affect the resistance of the wire and hence alter the current, such variation registering itself on the ammeter connected in the circuit.

The flow-meter was calibrated by absorbing the hydrogen sulphide in potassium hydroxide for a definite time interval, the amount of gas absorbed being measured by the increase in weight of the absorption bulb. For the lower rates, up to 0.2g. the time interval was taken as ten minutes; above this rate of flow five minutes was deemed sufficient. A calibration curve for the flow-meter was made by plotting the difference of the levels of the manometer against the weight of gas per ten minutes.

The reaction chamber was cleaned and dried thoroughly, connected to the remainder of the apparatus by a short rubber connection and immersed in a bath of melting ice. Hydrogen sulphide was passed through until all the air had been swept out. The pressure was regulated to the desired rate of flow and maintained constant by manipulation of stopcocks. The platinum filament was then heated and the reaction allowed to proceed for a short time until equilibrium was established. The hydrogen sulphide which was undecomposed came over with the hydrogen, the sulphur being condensed on the walls of the reaction chamber. The hydrogen sulphide was absorbed by

the potassium hydroxide while the hydrogen passed through the absorption system. From the increase in weight of the absorption bulb, the amount of hydrogen sulphide decomposed could be obtained by difference from the known rate of flow. The average of six results was taken at each rate of flow.

Experiments were carried out at four different temperatures, namely: 948°C., 1041°C., 1138°C., and 1269°C. One example of a typical run is reproduced and a summary of the results at other rates of flow follows. The graph shows the four curves obtained at the different temperatures plotting the weight of gas decomposed against the rate of flow of gas, each per ten minutes.

Results and Calculations

Temperature of filament 1138°C.
H_2S passing in 10 mins. 0.0847g.

Run	Wt. of bulb	Wt. after abs.	Wt. abs.	Wt. decomp.
1	37.9632	38.0327	0.0695	0.0152
2	38.0327	38.1027	0.0700	0.0147
3	38.1027	38.1729	0.0703	0.0145
4	38.1729	38.2428	0.0697	0.0150
5	38.3140	38.3844	0.0704	0.0143
6	38.3844	38.4544	0.0700	0.0147
			Average	0.0147

Experiment 1.

Temperature of filament 948°C.

Run	Flow of Gas	Wt. decomp.	Run	Flow of Gas	Wt. decomp
1	0.0740	0.0080	8	0.2310	0.0133
2	0.0847	0.0092	9	0.2772	0.0133
3	0.0955	0.0115	10	0.3219	0.0132
4	0.1058	0.0121	11	0.3430	0.0161
5	0.1268	0.0160	12	0.3661	0.0209
6	0.1448	0.0125	13	0.4086	0.0245
7	0.1732	0.0123	14	0.4462	0.0328

Experiment 2.

Temperature of filament 1041°C.

1	0.0591	0.0099	7	0.2018	0.0178
2	0.0835	0.0125	8	0.2278	0.0183
3	0.1058	0.0159	9	0.2534	0.0192
4	0.1250	0.0171	10	0.2782	0.0201
5	0.1418	0.0175	11	0.3262	0.0290
6	0.1736	0.0175	12	0.3714	0.0356
			13	0.4134	0.0427

Experiment 3.

Temperature of filament 1138°C.

Run	Flow of Gas	Wt. decomp.	Run	Flow of Gas	Wt. decomp.
1	0.0740	0.0142	10	0.1058	0.0204
2	0.0847	0.0147	11	0.1448	0.0253
3	0.0955	0.0179	12	0.1732	0.0242
4	0.1063	0.0214	13	0.2310	0.0299
5	0.1170	0.0237	14	0.2772	0.0336
6	0.1268	0.0250	15	0.3219	0.0379
7	0.1357	0.0242	16	0.3661	0.0471
8	0.1447	0.0254	17	0.4086	0.0518
9	0.1530	0.0248	18	0.4462	0.0564

Experiment 4.

Temperature of filament 1269°C.

1	0.1058	0.0234	6	0.2278	0.0359
2	0.1250	0.0260	7	0.2782	0.0433
3	0.1418	0.0267	8	0.3262	0.0505
4	0.1736	0.0295	9	0.3714	0.0570
5	0.2018	0.0326			

The temperature coefficient, per ten degrees, calculated for the rates of the reaction which are independent of the rate of flow of the gas, that is, for the horizontal portions of the curves, gives between 948°C and 1041°C a value of 1.034 and between 1041°C and 1138°C a value of 1.035. Taking 1.035 as the average value in this region, namely 1315°K, the heat of activation calculated from the Arrhenius equation

$$\frac{d \ln k}{dT} = \frac{E}{RT^2}$$

where k is rate of reaction, E is the heat of activation per gram molecule, R is the gas constant per gram molecule, T is the absolute temperature, yields a value of 11,750 calories.

Discussion of Results

The results may be best discussed by referring to the curves shown previously. The general upward trend of the curves shows an increase in the decomposition with increasing flow of the gas at any given temperature. In the absence of any complicating factors, such a behavior would be expected, producing a curve rising slowly to a maximum, which would correspond to maximum frequency of collision between the hydrogen sulphide molecules and the platinum filament. At this point any further increase of flow would have little or no effect on the rate of decomposition, as expressed by the amount decomposed per unit of time.

The absence of such a smooth curve is conclusive proof that the decomposition is not so simple as visualised above, but must be complex, in such a way

that the complicating factor is opposed in its effect to the increased decomposition with increased flow of gas. That this is so is readily seen from the horizontal portions of the curves where temporarily the rate of decomposition is constant for a small range in the rate of flow. What this complicating factor is may be judged best from the fact that eventually an increase in the rate of flow can overcome it, so that the normal increased decomposition with increased passage of the hydrogen sulphide is once more established. Furthermore that the increase in rate of flow necessary to cause this is less at higher temperatures than at the lower ones so that eventually at sufficiently high temperatures the complicating factor has almost entirely disappeared, seems significant.

From our knowledge of the poisonous nature of sulphur to catalysts, particularly of the platinum group, it would seem probable that the sulphur resulting from the decomposition was the cause of the complications to which reference has been made. The work of Maxted (loc. cit.) has definitely established that complexes between platinum and sulphur are formed and exhibit remarkable stability. The adsorbed sulphur however, could not be the cause of the decreased decomposition since a mere increase in the rate of flow of gas is sufficient to correct this. This latter fact is extremely significant suggesting that the sulphur, immediately after adsorption, or during that process, probably forms a thin film of vapor around the filament thereby preventing the on-coming hydrogen sulphide from reaching the hot surface. Accepting this fact, the effect of increased temperature is at once apparent, since then the rate of vaporisation of sulphur from the hot platinum surface would be greater.

It would appear therefore, that the actual mechanism of the complete reaction consists primarily of adsorption of hydrogen sulphide molecules on the platinum surface, a decomposition resulting in the separation of hydrogen and a subsequent desorption or vaporisation of the residual sulphur from the platinum surface. Such a mechanism is in agreement with our present knowledge and at the same time will explain satisfactorily the results found here.

Adsorption of H_2S by a platinum catalyst occurs as Maxted has shown with definite orientation, the sulphur being immediate to the platinum surface. The subsequent decomposition of the hydrogen sulphide molecule would cause, therefore, hydrogen to be liberated first, leaving sulphur momentarily attached to the platinum. That such attachment could hold for long is not probable owing to the high temperature of the filament. The sulphur therefore would be volatilised immediately, during which process the thin sulphur atmosphere referred to above would be formed. At any particular temperature the life of such an atmosphere would depend partly on the rate of flow of hydrogen sulphide and partly on the rate of decomposition. These two factors are opposed to one another from the point of view of removal of the sulphur atmosphere, since the increased decomposition increases it, whilst the increased rate of flow decreases it. As the rate of flow is increased however, there is a tendency also to increase the rate of decomposition.

If the rate of increase of rate of flow is greater than the rate of increase of decomposition, the removal of the sulphur atmosphere will eventually be accomplished, requiring however, a definite increase at a particular temperature for that purpose. As the temperature of the filament is raised the increasing decomposition with decreasing rate of flow will be accompanied by an increasing rate of evaporation of the sulphur, so that although at any given rate of flow the actual amount of sulphur formed is greater at the higher temperature, the rate of its removal from the sphere of action will also be greater and require therefore a smaller increase in the rate of flow to complete the removal. Such a mechansim explains satisfactorily the decreasing horizontal portions of the curves with increasing temperature, and their eventual disappearance when the temperature is sufficiently high.

Accepting this then, as the mechanism of the reaction there remains only one portion of the curves which will furnish any quantitative information with regard to the reaction. That portion, is the horizontal portion, for here alone are the two opposing factors, balanced. On the remainder of the curves the effect of a rise of temperature will be a complex funtcion made up partly of the temperature effect on the pure chemical decomposition and partly of the temperature effect on the rate of evaporation of the sulphur.

On the horizontal portion of the curves the rate of decomposition is a constant independent of the rate of flow of the gas. The temperature coefficient must therefore be due solely to the change in rate of evaporation of the sulphur. The value of 11,750 calories previously obtained is therefore the heat of evaporation of sulphur. Norrish and Rideal[1] have shown that the energy necessary to break a S-S bond is approximately 12,500 calories. It seems reasonable to assume, that the affinity between sulphur and platinum will be less than this value, although from Maxted's work such complexes seem highly stable. The value 11,750 calories therefore would appear quite reasonable and would lend confirmation to the suggested mechanism of reaction.

Summary

1. The decomposition of hydrogen sulphide on a heated platinum filament has been studied by a dynamic method, at four temperatures in the neighborhood of 1000°C.

2. The curves illustrating the relation between decomposition and rate of flow of gas at these temperatures have been found. These show three branches, two of which show an increased amount of decomposition as the rate of flow is increased, separated by a third branch where the amount of decomposition is constant and independent of the rate of flow. The extent of this branch decreases as the temperature rises, so that at the highest temperature the curve shows merely a point of inflexion.

[1] J. Chem. Soc., 123, 3216 (1923).

3. The mechanism of the reaction suggested, consists of the primary adsorption of the hydrogen sulphide oriented with the sulphur atom to the platinum, a splitting of the adsorbed molecule, hydrogen being liberated and subsequent evaporation of sulphur from the heated filament.

4. The temperature coefficient for the horizontal branches was found to be 1.035 per ten degrees which is equivalent at these temperatures to a heat of evaporation of sulphur from the platinum surface of 11,750 calories.

Havemeyer Chemical Laboratory,
New York, N. Y.

THE CATALYTIC ACTIVITY OF METALLIZED SILICA GELS
I. THE HYDROGENATION OF ETHYLENE*

BY VLON N. MORRIS AND L. H. REYERSON

As a result of the preliminary work on the catalytic activity of metallized silica gels, reported by Reyerson and Thomas[1] it was felt that a thorough study of some simple gas reactions would throw further light upon the behavior of these active catalysts. It was decided to first investigate in a quantitave manner the reaction between hydrogen and ethylene. Pease[2] lists several advantages in the use of this particular reaction. In addition to the reasons advanced by Pease for using this reaction it was felt that a comparison could be made between the usual catalysts and these metallized silica gels.

In carrying out this investigation it was decided to use the streaming method because it would then be possible to analyze the products accurately. In the case of many of the static methods reported in the literature the hydrogenation of ethylene is followed manometrically. While it is highly probable that the hydrogenation takes place no proof is often given that such is the case. A study of the effect of variation of the rate of streaming and the effect of continued use on the efficiency of the catalyst made this method desirable. Silica gels metallized with platinum, palladium, and copper were used in this investigation. Preliminary experiments with silverized gel showed that it had no catalytic effect on this reaction so no further work with the silver catalyst was undertaken. Variations in temperature, in the rate of flow of the gases thru the catalyst, and in the composition of the gas mixture were studied more or less independently of one another.

Experimental

The silica gel used in the preparation of these catalysts was prepared essentially as described by Patrick[3]. This silica gel was metallized by the method of Latshaw and Reyerson[4] except in the case of a part of the copper catalyst. Thorough outgassing of the silica gel was found to be essential before the hydrogen was admitted to the gel. Failure to do this resulted in diminished adsorption of hydrogen and a corresponding lack of reduction of metal ions to the metal. In the preparation of the platinized and palladized gels solutions of platinous and palladious salts were used. The solution containing the platinous ions was prepared by reducing a solution of chloro-

* The work described in this paper formed part of a thesis submitted to the Graduate Faculty of the University of Minnesota by V. N. Morris (Du Pont Fellow in Chemistry 1925-26) in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June 1926.

[1] "Colloid Symposium Monograph," 3, 99.

[2] J. Am. Chem. Soc., 45, 1196 (1923).

[3] U. S. Patent, 1297724.

[4] J. Am. Chem. Soc., 47, 610 (1925).

platinic acid by means of sulphur dioxide while the solution was hot. It was found that it was impossible to remove all of the sulphur dioxide from the solution and thereby prevent its appearance in the final product. The solution containing the palladious ions was prepared by dissolving ammonium chloropalladite.

In the case of the copperized gel one of the samples of catalyst was prepared as already indicated using a solution of cupric chloride. The reduction of the cupric ion is always incomplete under these conditions so that the product was dried and the reduction completed above 200° by hydrogen. The other samples of the copper catalyst were prepared by just covering the silica gel with N/5 copper nitrate solution and drying in an atmosphere of hydrogen and then completing the reduction with hydrogen above 250°. It was noticed rather early in the work that samples of the catalysts left exposed to laboratory air tended to change color. The platinized and palladized gels tended to change from black to gray black and then gray while the copperized gels usually became greenish in color. These changes were attributed to oxidation due to laboratory fumes. The catalysts were therefore kept in tightly stoppered bottles and no appreciable changes were noted under these conditions.

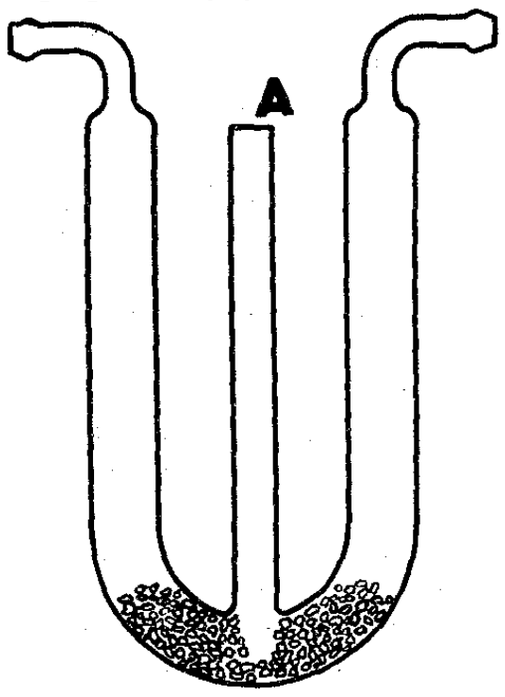


FIG. 1

In carrying out the catalytic hydrogenation the hydrogen and ethylene were first collected in the desired proportions in a four liter bottle by displacing water from the full bottle until water remained to a depth of about five centimeters. The water was forced from the bottle through a tube, into a reservoir above, by the pressure of the gases being introduced. The bottle was then thoroughly shaken to mix the gases and also to saturate the water. The gases were then forced through a drying tube and into the tube carrying the catalyst by means of water flowing from the reservoir above the bottle. A screw clamp on the tube connecting the reservoir with the bottle made it possible to regulate the flow of water and thereby control the volume of gas streaming through the catalyst per unit time.

The hydrogen used in these experiments was commercial electrolytic hydrogen and analyses showed it to be practically pure hydrogen. The ethylene used was obtained from the Ohio Chemical Company of Cleveland, Ohio. This gas analysed about ninety-eight percent ethylene. No attempt was made to remove the residual impurities except to bubble the gas through distilled water before collection in the four liter bottle.

From the bottle the mixed gas was passed through a calcium chloride drying tube and then through the tube containing the catalyst. The catalyst tube was made of Pyrex as shown in Fig. 1. The bottom of the tube was always filled with sufficient catalyst so that the gas mixture had to pass through the catalyst. The same amount of catalyst i. e. 3.5 grams was, used in each case. The shape of the catalyst tube made it possible to immerse the lower part of the tube in the various constant temperature baths used. A thermometer was inserted through tube A and the bulb of the thermometer was kept immersed in the catalyst. The thermometer was held in tube A by a section of rubber tubing. This sealed the top of the tube and prevented the escape of gases through this tube.

After passing the catalyst the gases were allowed to escape into the air for a few minutes until it was felt that the system had reached a steady state. The gases were then collected in a gas burette for purposes of analysis. The rate of flow of the gases was determined by the rate of collection in the gas burette. The reaction was followed by the determination of the ethylene content before and after reaction. These determinations were made by the usual methods of gas analysis. The disappearance of ethylene was checked from time to time by analysing for ethane formed. The results of these determinations showed that within the limits of experimental error the amount of ethane produced was equal to the amount of ethylene which had disappeared. As a typical experiment it was calculated from the amount of ethylene which disappeared that there should be 5.43 cc. of ethane in the gas sample. Actually 5.5 cc. were found. The agreement was thought to be close enough to prove that the product of hydrogenation was ethane. Blanks were always run on the gases used before each set of experiments and any slight corrections found were always included in the actual analysis of the products of reaction.

In carrying out the experiments a study of three variables was made. For the study of the effect of variation of the temperature a constant flow of gas through the catalyst was maintained at 60 cc. per minute. The catalyst tube was maintained at constant temperature throughout each run by immersing the tube in a constant temperature bath. Experiments were run at 0°, 30°, 60°, 90°, 150°, and 240°. The gas mixtures used in these determinations were those having twenty-five per cent or less of ethylene. For the experiments on the effect of variation of the rate of flow a temperature of 60° was chosen for the platinum and palladium catalysts and 240° for the copperized gel. This was done because copper had been found, during the first experiments, to be the most efficient at that temperature while the efficiency of the other two catalysts was as high at 60° as at any other temperature. Copperized gel prepared by the second method was used in the above experiments. Gas mixtures containing 33 per cent ethylene were used in this series of experiments with the hope that the efficiency of the catalysts might be diminished sufficiently to make noticeable the effects produced by changes of rate of streaming through the catalyst. The study of the effect of the variation of the composition of the gas mixtures was made at two tempera-

tures i.e. 27° and 170°. Copperized gel prepared by the first method was used in this set of experiments. The composition of the mixture varied from about 12 per cent ethylene to more than 80% ethlyene and the rate of flow was maintained at 100 cc. per minute. The tables give the actual percentages as determined by analysis in all cases.

Results

In determining the efficiency of the catalyst it has often been customary to neglect volume changes in the calculations. The efficiency of these catalysts was so great however, that large volume changes occurred and it was therefore necessary to take this into account in the calculations. The easiest method of handling this was to base the expressions on the percentages of ethylene present before and after reaction. Let a be the number of moles of ethylene in a given volume of the gas mixture before reaction and b the corresponding number of moles of hydrogen. If x is the fraction of ethylene hydrogenated then the number of moles of ethane, ethylene and hydrogen in the mixture after reaction will be ax, a−ax and b−ax respectively. If P_1 is the percentage of ethylene in the original mixture, and P_2 the percentage in the final mixture, it follows that

$$\frac{P_1}{100} = \frac{a}{a+b} \tag{1}$$

$$\frac{P_2}{100} = \frac{a-ax}{a-ax+ax+b-ax} = \frac{a-ax}{a+b-ax} = \frac{1-x}{\frac{a+b}{a}-x} \tag{2}$$

As a result of substituting the value of equation (1) in equation (2) we have the following:

$$\frac{P_2}{100} = \frac{1-x}{\frac{100}{P_1}-x} \tag{3}$$

From (3) the value of x comes out to be

$$x = \frac{P_1-P_2}{P_1} - \frac{(100).}{100-P_2}$$

This expression was used in all cases in which the ethylene constituted less than 50 percent of the gas mixture. In the cases in which the percentage of ethylene was greater than that of hydrogen the same equation was used except that the calculations were based on the percentages of hydrogen so that the terms of the equation had a different meaning.

Table I gives the results of the experiments on the effect of temperature variation on the efficiency of the catalysts. Each value given represents the average of from two to six determinations. The temperatures given are the temperatures of the catalysts at the time sampling was started. This temperature did not represent the actual temperature of the catalyst throughout the experiment as a rise of as much as 20° was noted on the thermometer

which was immersed in the catalyst itself. This was especially true at the lower temperatures. The results shown for copper represent the average of six separate determinations and the catalyst was prepared by the saturation of the gel with copper nitrate solution, followed by reduction with hydrogen. There was a variation of as much as two percent in the determinations on the copper catalyst so that six determinations were made and the results averaged.

TABLE I

The Effect of Temperature on the Hydrogenation of Ethylene in the Presence of Metallized Silica Gels

Temperature	Percentage of Ethylene		Percentage of hydrogenation
	Before reaction	After reaction	
	Palladized Silica Gel Catalyst		
240°	23.4	1.8	94.0
150°	23.4	0.7	97.7
90°	23.4	0.2	99.3
60°	23.4	0.1	99.7
30°	23.4	0.2	99.3
0°	23.4	0.2	99.3
	Platinized Silica Gel Catalyst		
240°	25.7	0.6	98.3
150°	25.7	0.5	98.5
90°	25.7	0.5	98.5
60°	25.7	0.4	98.8
30°	25.7	0.4	98.8
0°	25.7	0.4	98.8
	Copperized Silica Gel Catalyst		
360°	25	15.0	47.1
240°	25	11.8	59.9
150°	25	13.1	54.7
90°	25	13.9	51.6
60°	25	18.5	32.0
30°	25	22.4	13.5
0°	25	21.2	18.3
-20°	25	19.2	28.7

Fig. 2 represents the results of these experiments graphically. The determination at $-20°$ for the catalyst is of doubtful value because adsorption of ethylene is probably so great as to render the measurements inaccurate.

Table II gives the results of the study on the variation of the rate of streaming of the gas through the catalysts. The same catalysts were used as in the first experiments.

TABLE II

The Effect of the Rate of Streaming on the Activity of the Catalysts

Rate of Flow per minute	Percentage of Ethylene Before reaction	Percentage of Ethylene After reaction	Percentage of hydrogenation
	Palladized Silica gel catalyst at 60°		
52.2 cc.	32.2	0.1	99.8
127.7	32.2	1.2	97.4
200	32.2	2.5	94.5
316	32.2	3.4	92.6
	Platinized Silica Gel Catalyst at 60°		
57.7 cc.	32.2	1.3	97.2
103.6	32.2	3.9	92.5
171.4	32.2	7.3	83.4
273.0	32.2	9.1	78.6
600	32.2	10.4	72.1
	Copperized Silica Gel Catalyst at 240°		
22.0 cc.	32.9	10.5	74.8
92.3	32.9	20.8	43.8
240.0	32.9	25.6	26.2

Fig. 3 graphically represents these results.

Table III gives the results of the study on the variation in the composition of the gaseous mixture as it affects the activity of the catalysts at 27° and 170°.

TABLE III

The Effect of the Composition of the Gaseous Mixture in the Hydrogenation of Ethylene at 27°.

Percentage of gases before reaction		Percentage of Ethylene after reaction for each catalyst			Percentage of Hydrogenation for each catalyst		
Ethylene	Hydrogen	Palladium	Platinum	Copper	Palladium	Platinum	Copper
		Temperature of 27°					
15.7		0.5	0.4	13.7	97.4	97.9	14.7
23.9		1.1	0.6	23.6	96.5	98.1	1.3
49.2	46.2	20.4	19.4	48.7	75.4	77.1	2.0
72.9	22.3	72.8	72.0	72.8	0.5	5.5	0.5
		Temperature of 170°					
12.4		0.4	3.1	11.0	97.2	77.4	12.7
30.9		1.3	12.0	30.0	97.1	69.5	4.2
45.4		11.2	31.1	44.6	84.8	45.7	3.0
67.3	27.8	61.7	62.7	66.8	26.0	21.5	2.5
82.9	12.2	82.9	82.9	82.8	0.0	0.0	1.0

Figures 4 and 5 graphically represent the results of these experiments.

Discussion of results

The curves shown in Fig. 2 indicate a very normal behavior for the platinum and palladium catalysts. The slightly diminished activity at higher temperatures can no doubt be attributed to diminished adsorption. The curve for copper however is unusual. In all of the experiments minium activity was observed in the neighborhood of 30° and maximum activity at a temperature of 240°. A possible explanation of the behavior of the copper catalyst lies in the fact that a copper hydride may be forming. Adsorption measurements of Reyerson and Swearingen[1] show that the copperized gel does adsorb

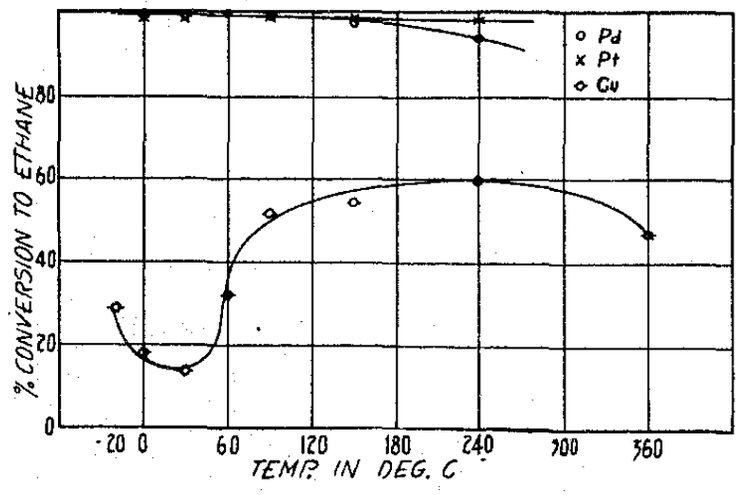


FIG. 2
The Effect of Temperature on the Catalytic Hydrogenation of Ethylene.

more hydrogen than silica gel itself at 0°. The copper of the catalyst is therefore adsorbing hydrogen. If the assumption is made that the copper is able to combine with this hydrogen under certain conditions to form a copper hydride and that this product is most stable at room temperature then we have a logical explanation of the behavior of the copper catalyst. Experiments were therefore carried out to confirm this assumption. An attempt was made to prepare the product, called copper hydride, by the usual method. This consists in mixing solutions of hypophosphorous acid and copper sulfate. An experiment was carried out at 0° and no precipitate had formed at the end of a two hour period. The mixture was then allowed to warm up to 10° for a period of six hours and still no precipitate formed. At the end of twelve hours the temperature had reached 22° and a precipitate had formed. If the solutions were mixed at room temperature a chocolate brown precipitate formed almost at once. At 100° a precipitate of a somewhat different color formed. These two precipitates were treated with concentrated hydrochloric acid. A vigorous evolution of gas occurred in the case of the precipitate formed at room temperature. The gas burned readily and gave every evidence of being hydrogen. Some metallic copper remained after treatment. The product prepared at 100° did not give enough gas to ignite when subjected to the same treatment and a larger residue of metallic copper remained. It is

[1] J. Phys. Chem., **31**, 88 (1927).

evident that the precipitate in both cases has some metallic copper in it and that a greater amount of material, capable of liberating hydrogen, is formed at room temperature than at 100°. A sample of the catalyst after being used at 30° was treated with concentrated hydrochloric acid. The metal deposit on the gel dissolved immediately with the evolution of some gas. The quantity of gas however was too small for testing. There was so little copper in the catalyst that this result was expected. However, the substance in the gel was completely dissolved as soon as the acid came in contact with it which would indicate that the copper had combined with the hydrogen.

These experiments indicate the probable formation of copper hydride in the catalyst, and that it is formed very readily at room temperature. Such formation during the process of catalysis would no doubt cut down the activity of the catalyst. As the experiments indicate at higher temperatures less hydride is formed. Futhermore any hydride that formed would be less stable as the temperature increased. Hydrogen liberated by decomposition would be likely to react as it was liberated. Thus at higher temperatures the combined effect, of catalysis due to adsorption by copper itself and the reaction resulting from the hydrogen liberated by hydride decomposition, would appear.

The experiments on the change of rate of flow indicate a fall in efficiency with increased rate of streaming through the catalysts. The fall in efficiency is not very great however for the platinum and palladium catalysts. In the case of copper the efficiency diminishes considerably as the space velocity increases. These results, as well as much of the work presented in this paper, find explanation in the idea that the most active areas in a catalyst material are those having atoms in an unsaturated or extra lattice condition.[1] The method employed in the production of the platinum and palladium catalysts must of necessity produce a great number of metal atoms, on the silica gel surface, which are not in the crystal lattice of the metal. Thus the catalysts would be expected to be very active and such is the case. X-ray analysis of these catalysts, as reported by Reyerson, Harder and Swearingen,[2] tends to confirm this point of view. The copper catalyst was not produced in the same way since reduction was always completed at higher temperatures whether the first reduction was by adsorbed hydrogen or not. This would reduce the number of active centers since the metal atoms nearest the gaseous conditions would distill to a less active condition. Under like conditions the efficiency of the copperized gels has always been found to be less than that of the other two catalysts. The curve shown for the copper catalyst in Fig. 3 is therefore to be expected.

The curves in Figs. 4 and 5 show conclusively that the efficiency of the catalysts is inversely proportional to the partial pressure of ethylene. The palladium and platinum catalysts show zero efficiency before the gas mixture

[1] See, for example, "Fourth Report of the Committee on Contact Catalysis." Taylor: J. Phys. Chem., 30, 145 (1926).

[2] J. Phys. Chem., 30, 1623 (1926).

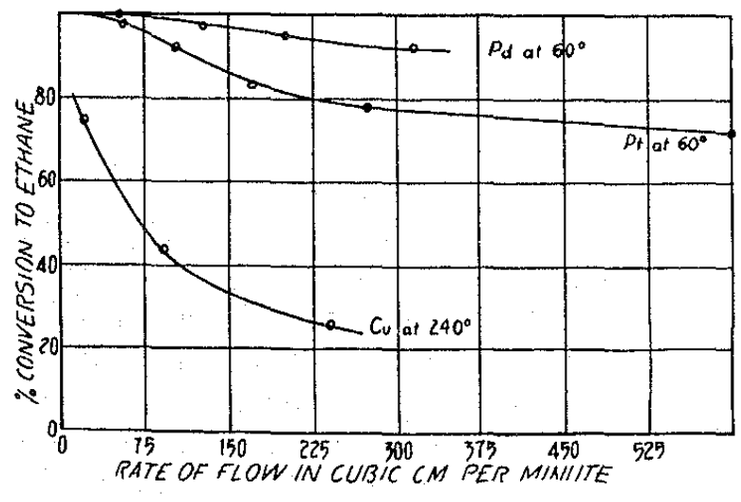


FIG. 3
The Effect of Rate of Flow of the Gaseous Mixture.

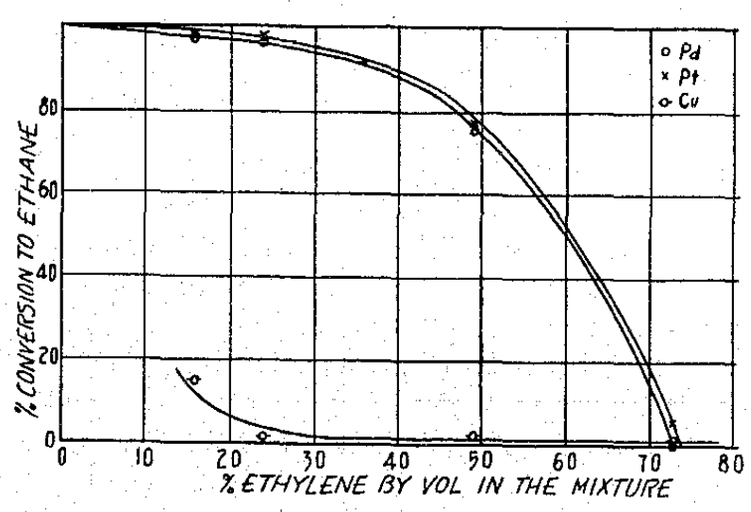


FIG. 4
The Effect of Variation in the Reaction Mixture at 27°C.

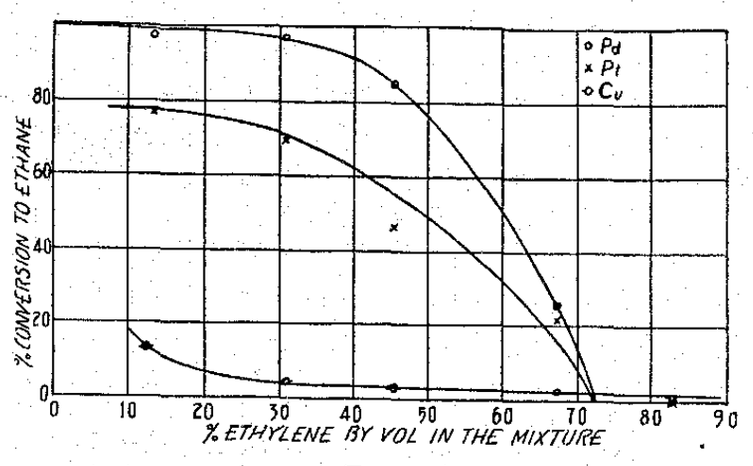


FIG. 5
The Effect of Variation in the Reaction Mixture at 170°C.

becomes eighty per cent ethylene. The logical explanation of these results is found in the proposals of Langmuir[1]. The ethylene molecules which are adsorbed are oriented on the surface of the catalyst so that they will no longer react with the hydrogen molecules which strike the surface. On the other hand the hydrogen molecules which are adsorbed on the surface are capable of reacting with the ethylene molecules which strike the surface. Ethylene is much more strongly adsorbed by these catalysts than is hydrogen. Therefore, as the partial pressure of ethylene is increased, the fraction of the surface covered by ethylene molecules increases very rapidly. The active centers of the platinum and palladium catalysts thus appear to be completely covered with ethylene molecules while the partial pressure of hydrogen is still nearly one-fourth of the total gas pressure. The copper catalyst does not reach zero activity in the experiments as carried out in this investigation. This is probably due to the fact that the active copper surfaces do not hold the ethylene molecules so firmly. Another explanation for the observed results may be that suggested earlier in this paper to account for the unusual behavior of copper, that is the formation of copper hydride. A small amount of copper hydride forming and decomposing may account for the slight activity of the copper which persists after the platinum and palladium catalysts had ceased to act.

Summary

1. Platinized and palladized silica gels show marked activity as catalysts in the hydrogenation of ethylene over a considerable range of temperatures.

2. Copperized silica gel shows an unusual and variable activity in the same reaction. The possibility of hydride formation is suggested in explanation of this behavior.

3. The efficiency of these catalysts is inversely proportional to the partial pressure of the ethylene in the gaseous mixture.

The School of Chemistry,
University of Minnesota,
Minneapolis, Minnesota.

[1] Trans. Faraday Soc., 17, 607, 621 (1921-22).

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THE FUNCTION OF WATER PRESENT IN SILICIC ACID GEL– THE STRUCTURE OF SILICIC ACID GEL

BY H. A. FELLS AND J. B. FIRTH

One of the problems of colloid chemistry is the actual cause of colloidality, which is intimately connected with the ultimate structure of the substances in gel form.

In the case of silicic acid gel, this problem has received attention from very early times and was introduced by Baumé[1] when he referred to the union of particles of SiO_2 and to the change which occurred in a gel according to its method of preparation and the age at which it was investigated.

Van Bemmelen[2] was one of the earliest workers to actually formulate a conception of a particular internal structure of silicic acid gel, when in 1896, he suggested a cell-like structure. Two years later he attributed this cell-like structure to the separation of the colloid into two liquids; one, the hydrogel, which has the greater vicosity and forms a network or honeycombed structure which retains the other liquid in the cells and in the interstices between the cells. The hydrogel, he stated, was an intermediate stage in the passage from the liquid to the "rigid" state during the separation of a dissolved substance in the colloidal form from its solvent. The formatiom of the hydrogel is indicated by coagulation.

In his first paper, van Bemmelen also showed that the water present in the gel could be removed gradually by desiccation, the water could also be re-absorbed in a similar continuous manner. The curves for dehydration did not however follow the same path. Again, he observed that dehydration became increasingly difficult as the anhydrous condition was approached. During the process of rehydration a point is reached at which the gel becomes opaque, but beyond this point it again becomes transparent. In another paper van Bemmelen[3] showed that on partial ignition, the power of rehydration was diminished, whilst after prolonged ignition this power was lost altogether; the density of the gel, however, was thereby decreased indicating that the network of spaces had been destroyed.

In 1911 Zsigmondy[4], from vapour pressure measurement, calculated the diameter of the pores in silicic acid gel to be only $5\mu\mu$. The peculiarity of dehydration and rehydration cited by van Bemmelen he attributed to the fact that water fails to wet the walls of the capillaries during the process of rehydration owing to the presence of air in the capillaries. That the "dried" gel could not be made to re-assume the initial heavily hydrated condition he attributed to

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[1] "Chimie Experimentale" **1**, 329 (1773).
[2] Z. anorg. Chem., **13**, 233 (1896); **18**, 14 (1898).
[3] Arch. néerl., **6**, 607 (1901).
[4] Z. anorg. Chem., **71**, 356 (1911).

the union of amicronic particles of silica to form larger particles, probably crystalline. (Compare Baumé, Schwartz and Liede[1], and Bradford.[2])

Anderson[3] confirmed Zsigomdy's measurement of the pore diameter and showed also that the opaque phase produced in the rehydration of the gel was not due to the formation of a definite hydrate. Tschermak[4] stated that the opacity is due to a definite hydrated phase.

Vanzetti[5] studied the action of low temperatures on silicic acid gel in freezing out the water and found that the final ratio of silica to water depended upon the initial concentration. He also observed that greater dehydration was possible with older gels. He maintained that his results did not favour the existence of definite hydrates in the gel. The following year Vanzetti repeated his experiments at lower temperatures (to −200°C) and he showed that the final composition of the gel was independent of the temperature of freezing, a result which supported the *granular* theory of gel structure. While the state of the last traces of water, not removable by freezing could not be definitely decided, the results showed a tendency towards the separation of anhydrous silica.

Lenher[6] showed that the water present in the gel could be lowered very much by pressure. He also found that finely divided sand (particles less than 0.004 mm.) when heated under pressure in presence of excess of water at 300°-450° formed a gel containing 15-18 per cent water. The hydration of fused quartz could be brought about in a similar manner and he considered that the action of water was that of a solvent, producing silica gel and causing it to go into the colloidal form. Lenher concluded that silicic acids should be regarded as conforming to a general formula $xSiO_2yH_2O$ in which the quantities of water can vary from a true solution of silica in water successively through highly hydrated gels, which by pressure alone may be converted into gels having only a small percentage of water.

The observations of Schwartz and Liede in an investigation on the ageing and transformation of silicic acid gel showed a close resemblance to certain postulations made many years previously by Baumé. They concluded that the ageing process consisted of the concentration of $(SiO_2)_x$ molecules to $(SiO_2)_{2x}$ molecules, and that this occurs without any changes in the appearance of the gel. This type of change proceeded still further, with time, leading to the formation of $(SiO_2)_{3x}$ molecules which was indicated by the transparent gel becoming opaque. This same phenomenon was observed when the gel was dehydrated quickly by heat, but *for some unexplained reason* a much greater loss of water seemed to be essential before the same end point was reached. Arsem[7] expressed the view that a gel consisted of two phases, (a)

[1] Ber., **53**, B 1509 (1920).

[2] Science, (1) **54**, 463 (1921); Biochem, J., **11**, 14 (1917); **12**, 351 (1918); **14**, 91 (1920); **15**, 353 (1921); **17**, 230 (1923).

[3] Z. physik. Chem., **68**, 191 (1914).

[4] Monatsheft, **33**, 1087 (1912).

[5] Atti Inst. Veneto Sci., **75**, 261 (1915); **76**, 287 (1916).

[6] J. Am. Chem. Soc., **43**, 391 (1921).

[7] J. Phys. Chem., **30**, 306 (1926).

the associated phase, (b) a free phase "The 'associated phase' is made up of molecular units held in combination by the same kind of forces as those which function in the formation of a crystal lattice." The forces holding the molecular units together are the residual valencies of the units, and only a portion of these valencies is used. Consequently, the associated phase is much extended and of loose structure, an intermediate stage in the formation of a crystal lattice, and will contain voids of practically molecular dimensions. The "free phase" fills the voids in the associated phase and the gel is therefore composed of these two separate phases, the one solid, the voids of which are filled with the second phase. The phenomena of segregation, shrinkage, and syneresis can be explained by the mutual satisfaction of the remainder of the residual valencies, with consequent loss of voids and ultimate tendency to form a crystal lattice. Arsem considers that a "crystal containing included liquid may contain a proportion of gel structure."

The foregoing brief survey of the researches on the functions of the water present in the gel of silicic acid show that since the very earliest times, this problem has received very considerable attention. The outcome of all the work has resulted in a division of opinion as to the existence of definite hydrates of silica during the formation of the gel.

Experimental

The purpose of this series of experiments was to find further evidence from which some more definite conclusion might be arrived at, as to the existence of definite hydrates during gel formation.

A sol was prepared by adding 70 cc. of sodium silicate solution, D = 1.181 to 100 cc. of hydrochloric acid, of a strength 2.911N. Local coagulation of the mixture was prevented by agitating well with a mechanical stirrer during mixing. Both the sodium silicate and hydrochloric acid were of a high degree of purity. After the mixture has been cooled to room temperature, equal quantities of the mixture were weighed out into clean glass petri dishes. These dishes were all of the same size, and were covered with a glass lid to prevent loss by evaporation, thus each one gave as nearly as possible the same surface area of evaporation. Each portion of the sol mixture was then allowed to assume the gel form, the intention being to investigate the influence of time on any existing state of combination of the water present with the silica. The gels were all kept at room temperature, and after definite intervals, one of the portions was weighed and transferred to a vacuum desiccator over sulphuric acid. Desiccation was allowed to proceed until crystals of sodium chloride could be detected on the surface and the gel[1] was then immediately reweighed.

The difference between these two weighings gave the amount of water extracted from the gel by the sulphuric acid. The gel was now dried to a constant weight in the steam-oven, and the silica estimated by washing out the sodium chloride by repeated treatment with hot water, and finally heating the residual silica at 900°C, until a constant weight was obtained.

[1] Cf. Fells and Firth: Proc. Roy. Soc., 112 A, 468 (1926).

An analysis of the original sodium silicate gave

$$Na_2O;\ SiO_2 = 0.81 : 1.618$$

From this analysis of the water-glass, and the amount of silica present in each portion of the gel investigated, it was possible to determine the weight of sodium chloride in each portion of gel. The free acid remaining in the gel was determined (a) indirectly by determination of total chlorine (b) directly by the determination of the free acid extracted from the gel. In all cases the residual gel contained, even after prolonged extraction small traces of chlorine. The data, therefore, which could be obtained for each gel portion, were:—

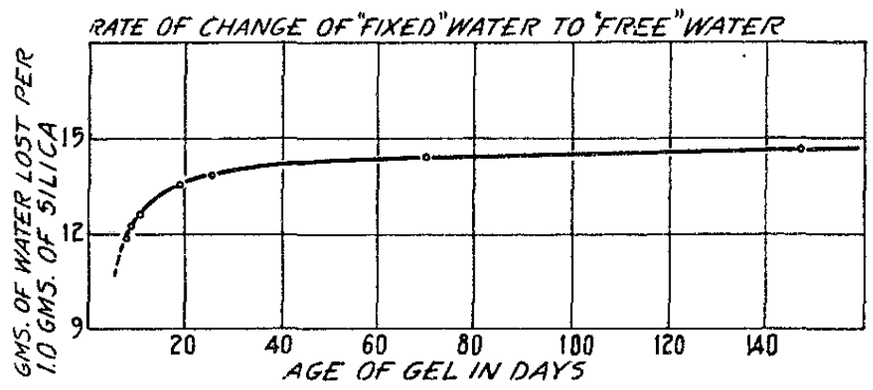


FIG. 1

a. Total amount of anhydrous silica.
b. " " " sodium chloride
c. The amount of water lost by desiccation, up to the point at which sodium chloride first appeared.
d. The amount of water remaining.
e. The free acid remaining in the gel.

The results of a typical series of determinations on one gel are given in tabular form, and the figures are corrected to correspond with 1.0 gms. of anhydrous silica, for comparison. The results are shown graphically in Fig. 1. It will be observed from column 2, that during the period of ageing, the loss of water escaping due to evaporation was comparatively small, *i. e.*, the gel had been efficiently protected from air evaporation.

It is apparent from Table I that the amount of water lost up to the particular point at which crystals of sodium chloride appear, increases as the gel portions increase in age. This observation is in strict agreement with that of B. L. Vanzetti, who found that a more advanced dehydration could be obtained by the influence of low temperatures upon an old gel than a new one. This same phenomena had been mentioned much earlier by van Bemmelen. Vanzetti was of the opinion that this observation did not favour the hydrate conception, but supported the capillary theory.

Although the experiments just described are very simple, the results obtained are of a very striking nature. Under similar conditions the concentrations of the sodium chloride must be the same at the point at which crystallization begins. It must be noted that the concentration of the sodium

TABLE I

Results corrected to a weight of gel, of 1.10 gm. SiO_2 content.

Age of gel in days	Total weight of gel when introduced into desiccator	(a) Water lost by gel, (b) remaining in the gel at the instant* of the appearance of sodium chloride needles. (a) Water lost	(b) Free Hydrochloric acid
7	20.954	11.905	0.0818
7½	20.894	12.203	0.0800
9	20.844	12.490	0.0774
12	20.724	12.682	0.0791
19	20.984	13.711	0.0782
26	20.884	13.800	0.0766
70	20.924	14.660	0.0768
147	20.904	14.917	0.0738

* In order to determine this point, two similar gels were placed in the desiccator with an interval of two hours between; when crystals were observed on the first gel. The second gel was examined more carefully at intervals of thirty minutes.

chloride will not be uniform throughout the gel, but will tend to concentrate at the surface of the gel, that is, at the open ends of the capillaries from which solvent is being lost.[1] It will be apparent therefore that crystallization will take place at the open end of the pore; and in the present investigation the formation of crystals[2] at the surface is used only as an *indicator*, to mark the attainment of a certain definite concentration at the pore. The more dilute the salt solution the greater will be the loss of water by evaporation before the crystallization point is reached.

From the results it will be observed that the amount of water withdrawn by the sulphuric acid from the silicic acid gel, before the crystals of sodium chloride appear, increases in amount as the gel increases in age. This would mean that with age the solution of sodium chloride within the gel was becoming less concentrated. As the amount of sodium chloride cannot change, it is apparent that the amount of water acting as solvent for the salt must be increasing. It is on this fact that the following conception of the status of water in silicic acid gel is based; and also the explanation of the presence of a capillary structure in the firm gel.

In the authors' opinion, the water present in silicic acid gel, formed by adding a solution of sodium silicate to hydrochloric acid, is functioning in *two* separate and distinct capacities.

These two functions may be used to give names to the two capacities.

[1] Fells and Firth: Proc. Roy. Soc., **112A**, 472-4 (1926); Kraus: Kolloid-Z., **28**, 161 (1921).

[2] A gelatin gel containing sodium chloride was prepared and the gel dehydrated exactly as described above for silicic acid gel. In this case globules of liquid collected on the surface, which as the dehydration proceeded ultimately gave rise to the normal cubic crystals of sodium chloride; no needle-shaped crystals were detected.

A. 'Fixed' water. B. 'Free' water.

The 'fixed' water is a certain varying amount of the total water in the gel, which is definitely associated with the silica.

The 'free' water is the remainder of the total water not acting as 'fixed' water. It is free, in the sense that it is only enclosed in the meshes or pores of the gel, or interstices between adjacent hydrated particles. It is capable of acting as solvent for the sodium chloride present, and be easily removed by desiccation over sulphuric acid. The 'fixed' water cannot be so easily removed, and cannot, as such, act as solvent for the sodium chloride.

As the amount of 'free' water, acting in a solvent capacity continuously increases, and there is only one source from which this increase can be obtained, and that is, the 'fixed' water, and it would appear that the ageing process consists of a change of the 'fixed' water to 'free' water.

It may be argued that the increase in the amount of water extracted by the sulphuric acid, is caused by the tendency of the salt to form a supersaturated solution, owing to an internal pressure set up by the contraction of the gel. It should be pointed out that the crystals of the sodium chloride are produced, not *in* the gel, but at the the surface, so that the solution from which the salt crystals appear is under normal atmospheric pressure, no matter what the pressure *inside* the gel may be.

The phenomenon of sudden crystallization characteristic of super-saturation of a solid in a liquid was at no time observed in these experiments. Any tendency there may be for super-saturation to occur is minimised by the presence of hydrochloric acid which is in excess; the only factor involved is the concentration at the *pore* or open end of the capillary[1], and the condition required for crystallization will be similar in all cases.

This suggestion of 'fixed' changing to 'free' water is therefore based upon the increasing amount of water acting as solvent for the salt.

The presence of free hydrochloric acid does not in any way detract from the general argument that the amount of 'free' water is continuously increasing. The initial free acid is the same in *all* cases, and the values at the instant of crystallization are very similar, hence the effect of the hydrochloric may be regarded as uniform throughout the series. A probable sequence for this series of changes may be described as follows.

The moment the sol mixture is prepared, the silica is produced in a very widely dispersed condition, *i. e.*, molecular. These molecules of silica tend to unite, by reason of the forces which tend towards the formation of a crystal lattice, because there are residual valencies. It has been shown by R. Schwartz and O. Liede that the hydrated molecules of SiO_2 do aggregate into larger molecules, in the manner

$$(SiO_2)_x \rightarrow (SiO_2)_{2x} \rightarrow (SiO_2)_{..x}$$

In the initial widely-dispersed condition of the SiO_2 molecules, it is possible for each separate molecule to become heavily hydrated, by the union of units of SiO_2 and H_2O. That is, the residual valencies of the SiO_2 molecules are

[1] Cf. Fells and Firth: loc. cit.

first satisfied by the units of water available, with the result that a silicic acid complex having a large number of molecules of water is formed. As this process takes place, there will be formed many such heavily hydrated molecules of silica, which, however, are free. At the same time, the viscosity of the solution will increase.

In the course of time, the forces tending to unite the silica molecules will orientate themselves, and so those forces holding the water will weaken and the water be set free.

These changes are fairly rapid in the new mixture, causing the sol to become increasingly viscous, and this increase in viscosity will ultimately cause the gel form to appear. The loss of water is coincident with, and dependent upon the tendency of the hydrated SiO_2 molecules to take up definite orientation, the *final* orientation being that of the crystal lattice. It has been observed by Bradford that ultimately, silicic acid gel does change into quartz, which is anhydrous.

It may be said, therefore, that it is the primary tendency to form a complex hydrate of silica, and the secondary tendency for the orientation of the hydrated SiO_2 molecules, which make it possible for silicic acid gel to exist. *It may also be argued that the silica cannot exist in the gel form without the primary formation of true hydrates of silica.*

This suggested formation of hydrates does not detract from the theory of the presence of capillaries in the hard gel, but rather does it give a reason for the appearance of capillaries, from an original 'homogeneous' solution. Up to the present, no reason has been forthcoming for the formation of a structure so easily demonstrable in the hard gel.

If the formation of chemical hydrates is accepted, the formation of capillaries seems to be a natural consequence. The original mass of the newly formed gel consists of molecules of heavily hydrated silica. As the silica begins its slow course of crystallization, with the loss of water, a very loose structure, containing large meshes like a sponge, will be formed.

The 'free' water will fill these meshes, which are all connected. This is the beginning of the structure, which, as the gel ages, becomes a more clearly defined, and in the 'dried' gel, is said to be of, a capillary nature, owing to the enormous contraction of the gel.

University College,
Nottingham.
April 27, 1927.

THE RÔLE OF WATER IN THE PHOTOCHEMICAL DECOMPOSITION OF ZINC SULFIDE

BY HARRY B. WEISER AND ALLEN D. GARRISON

Zinc sulfide alone is sometimes employed as a pigment but its use for this purpose is confined pretty largely to lithopone which is an intimate mixture of zinc sulfide and barium sulfate prepared in a special way. The process for preparing lithopone consists in the double decomposition of barium sulfide and zinc sulfate in solution, followed by igniting the sulfide-sulfate precipitate and quenching in water. Before ignition, the precipitate is useless as a pigment, having very little covering power or body. Heating changes the physical character of lithopone: first, by dehydrating the zinc sulfide; second, by rendering the mass brittle so that fine grinding is possible; and third, by increasing the density and thereby increasing the body of the pigment. Unless special precautions are taken in the manufacture of lithopone it darkens in the sunlight but becomes white again in the dark. Attention was first called to this phenomenon by Phipson[1] who observed that a gate-post painted white with a lithopone paint turned dark during the day and became white again at night. The barium sulfate in lithopone is without influence or plays but a minor role in the process since zinc sulfide alone will exhibit the same phenomenon. The blackening in ultraviolet light is due to finely divided metallic zinc which is formed along with sulfur by the photochemical decomposition of the salt.[2]

Conditions for Photochemical Decomposition

Zinc sulfide precipitated from ammoniacal solution with hydrogen sulfide or ammonium sulfide consists of minute cubic crystals corresponding to zinc blende or sphalerite. Under ordinary conditions, the precipitated sulfide is stable but is rendered light-sensitive by ignition under such conditions that wurtzite is formed. A second requirement for light-sensitivity is the presence of an excess of water. Specially prepared, chemically pure zinc sulfide[3] will darken, so that impurities are not essential to the process although certain salts, especially soluble zinc salts, increase the light-sensitivity. Indeed, we have found that an unignited zinc blende formed slowly from slightly acid solution will darken on exposure to light in contact with a zinc chloride solution.

The much greater light-sensitivity of wurtzite was recognized thirty-five years ago by Cawley[4] who pointed out that zinc blende will not darken in ultraviolet light. This conclusion was confirmed recently by Schleede[5] from

[1] Chem. News, **43**, 283; **44**, 73 (1881).

[2] Cawley: Chem. News, **44**, 51, 167 (1888); O'Brien: J. Phys. Chem., **19**, 113 (1915); Durst: Z. angew. Chem., **35**, 709 (1922); Job and Emschwiller: Compt. rend., **177**, 313 (1923).

[3] Tomaschek: Ann. Physik, (4) **65**, 189 (1921).

[4] Chem. News, **63**, 88 (1891).

[5] Z. physik. Chem., **106**, 391 (1923).

observations with pure precipitated zinc sulfide thrown down from alkaline solution. When ignited below 850° the sulfide was not darkened by long exposure to quartz ultraviolet light and an x-radiogram showed it to consist of the cubic crystals of sphalerite. Ignition at 1150° (35° below the melting point of wurtzite) gave a product with the maximum light-sensitivity and an x-radiogram showed it to be hexagonal wurtzite. Ignition at 1000°, gave a mixture of both blende and wurtzite which darkened less readily than pure wurtzite. The presence of copper, manganese, or cadmium in amounts necessary to cause phosphorescence had no effect on the light-sensitivity.

By carrying out the ignition in the presence of a flux, Schleede found the ignition temperature to be of secondary importance. Thus when the sulfide was ignited at as low a temperature as 750° in the presence of potassium chloride, an x-radiogram showed the formation of some wurtzite and even glass ultraviolet light caused darkening. Since Schleede did not know the mechanism of the darkening process, he attributed the light-sensitivity in the presence of chloride to the formation of mixed crystals of wurtzite and the halogen. Washing out the chloride destroyed the sensitivity to glass ultraviolet light but did not affect the action toward quartz ultraviolet light. Ignition with both chlorides and bromides gave light-sensitive products but ignition with fluorides, phosphates and borates gave light-stable preparations. This is in line with O'Brien's[1] findings, that the addition of phosphates, ferrocyanides, borates, cyanides, or bicarbonates to lithopone prevented the darkening or decreased it to an appreciable extent.

Cawley,[2] who suggested that the darkening of zinc sulfide was due to metallic zinc and who first pointed out that ordinary zinc blende is non-sensitive to light, likewise was the first to recognize the importance of the presence of moisture for the blackening. Recently Lenard[3] and Schleede[4] called attention to the fact that more than a trace of moisture is necessary. Indeed the blackening is more marked when the surrounding air is supersaturated with moisture than when it is saturated; and the effect is still more pronounced when the sulfide is covered with water.

A number of hypotheses have been put forward to account for the action of water. Since a trace of the liquid is insufficient to bring about photochemical decomposition it is improbable that the liquid plays a catalytic rôle similar to that in the thermal decomposition of ammonium chloride.[5] Lenard[6] assumes that the action of water is purely mechanical, forming a film around sulfur atoms in so-called "center molecules" and thus slowing down the recombination of the sulfur atoms with "loosened" zinc atoms. This hypothesis was found to be untenable since no darkening takes place on exposing a sensitive sulfide to light in the presence of thoroughly dried liquids

[1] J. Phys. Chem., **19**, 113 (1915).
[2] Chem. News, **63**, 88 (1891); Cf. O'Brien: J. Phys. Chem., **19**, 126 (1915).
[3] Ann. Physik, (3) **68**, 572 (1922).
[4] Z. physik. Chem., **106**, 390 (1923).
[5] Baker: J. Chem. Soc., **65**, 611 (1894).
[6] Ann. Physik, (4) **68**, 572 (1922).

such as carbon tetrachloride, carbon bisulfide and benzene which are solvents for sulfur. Maass and Kempf[1] suggest that the water is photochemically decomposed giving nascent hydrogen[2] which reduces the zinc sulfide. This suggestion seems very far-fetched, since either nascent oxygen[3] or hydrogen peroxide[4] would be formed simultaneously and would counteract the reducing action of any nascent hydrogen. Maass and Kempf suggest further that the blackening is due to reduction by formaldehyde formed by the action of light on moist carbon dioxide.[5] We have found this view to be untenable since blackening was observed when the formation of formaldehyde was eliminated by taking special care to remove carbon dioxide from the sensitive sulfide and the water in contact with it.

It thus appears that the various hypotheses which have been put forward to explain the rôle of water in the photochemical decomposition of zinc sulfide, are either impossible or improbable. A more reasonable explanation of the effect of water was reached from a consideration of the mechanism of the process of decomposition which will be taken up in the next section.

The Mechanism of the Decomposition Process

Since zinc sulfide which has not been ignited will not blacken ordinarily, Cawley suggested that the ignition results in the formation of some zinc oxide with which the remaining zinc sulfide reacts in the light, as follows: $ZnS + {}_2ZnO \rightarrow SO_2 + {}_3Zn$. This view is untenable since ignition of lithopone under conditions for forming a film of zinc oxide over the sulfide particles give a light-stable product while removal of the zinc oxide film from such a preparation by heating with an acid, restores the light sensitivity.[6] Furthermore, chemically pure zinc sulfide is darkened by light. Maass and Kempf believe that the darkening is occasioned by the following reaction: ${}_2ZnS \rightarrow ZnS_2 + Zn$. This is likewise untenable since sulfur instead of the hypothetical zinc disulfide is formed in the process.

Lenard explains the necessity for ignition by postulating the formation of polymerized molecules of $(ZnS)_x$ which are assumed to blacken owing to the "liberation or loosening of zinc atoms from the molecular union." The subsequent discoloration in the dark is attributed to the recombination of the loosened zinc and sulfur atoms. This mechanism is not satisfactory since it is based on certain assumptions of doubtful accuracy and since it does not accord with all of the experimental observations. In the first place, the formation of polymerized molecules of zinc sulfide has not been proven. Moreover, it is questionable whether a "loosened" atom of zinc would cause darkening and we know definitely that free atoms of zinc are formed. Lenard's "loosened" zinc atoms would seem to be comparable to the sensitized atoms

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[1] Z. angew. Chem., **36**, 294 (1923).
[2] Berthelot and Gaudechon: Compt. rend., **150**, 1690; **151**, 395 (1910).
[3] Thiele: Ber., **40**, 4914 (1907).
[4] Kernbaum: Compt. rend., **152**, 1668 (1911).
[5] Berthelot and Gaudechon: Compt. rend., **150**, 1169, 1327, 1517, 1690 (1910).
[6] O'Brien: J. Phys. Chem., **19**, 113 (1915); Maass and Kempf: Z. angew. Chem., **36**, 294 (1923).

of silver in the latent image, which cause no visible change in the appearance of the photographic plate until they are set free by a reducing agent. Finally, Lenard's assumption that the blackening-discoloration process is reversible, is not in accord with the experimental facts to be recounted in the next section.

It has been known for a long time that a soluble silver salt such as silver nitrate increases the light-sensitivity of silver bromide[1] and Cawley[2] and O'Brien[3] observed a very marked increase in sensitivity of lithopone in the presence of soluble zinc salts. The sensitizing action of silver nitrate on silver bromide has been accounted for[4] by assuming that the soluble salt acts as a bromine acceptor reacting with the latter in accord with the equations $Br_2 + AgNO_3 + H_2O = AgBr + BrOH + HNO_3$; but no such mechanism can be assumed for the sensitizing action of zinc chloride on lithopone. The recent investigations of Fajans[5] disclose, however, that silver nitrate not only plays the secondary role of a bromine acceptor but it influences the primary light process. The mechanism is as follows: Lottermoser[6] showed that silver ions from silver nitrate solution are preferentially adsorbed by silver bromide imparting to the salt a positive charge. Fajans and Frankenburger[7] measured this adsorption quantitatively and found that every fourth to tenth atom of bromine in the surface of the silver bromide particles had adsorbed a silver ion from a solution of silver ions as dilute as 1.8×10^{-5} molar. At higher concentrations it is probable that all the bromide atoms in the surface would be covered by adsorbed silver ions giving a crystal with the maximum positive charge.

Since silver bromide crystals belong to the cubic system it may develop its [100] faces only and give cubes or it may develop other faces giving octahedra.[8] Thus the crystals which form from ammoniacal solution show [111] surfaces only.[9] The cross-section of a portion of silver bromide particles of the cubic form and of the simplest octahedral form, may be represented diagramatically as follows: (I) when no ions are adsorbed; (II) when every third or fourth bromine atom in the surface has adsorbed a silver ion and (III) when every third or fourth silver atom in the surface has adsorbed a bromine ion. The silver atoms are designated by +, the bromine atoms by −, and the respective adsorbed ions by $Ag^{\cdot}$ and Br'.

I. Before adsorption of any ions:

[1] Vogel: Ann. Physik, **119**, 497 (1863).

[2] Chem. News, **63**, 88 (1891).

[3] J. Phys. Chem., **19**, 127 (1915).

[4] Plotnikow: "Allegemeine Photochemie," 246 (1920).

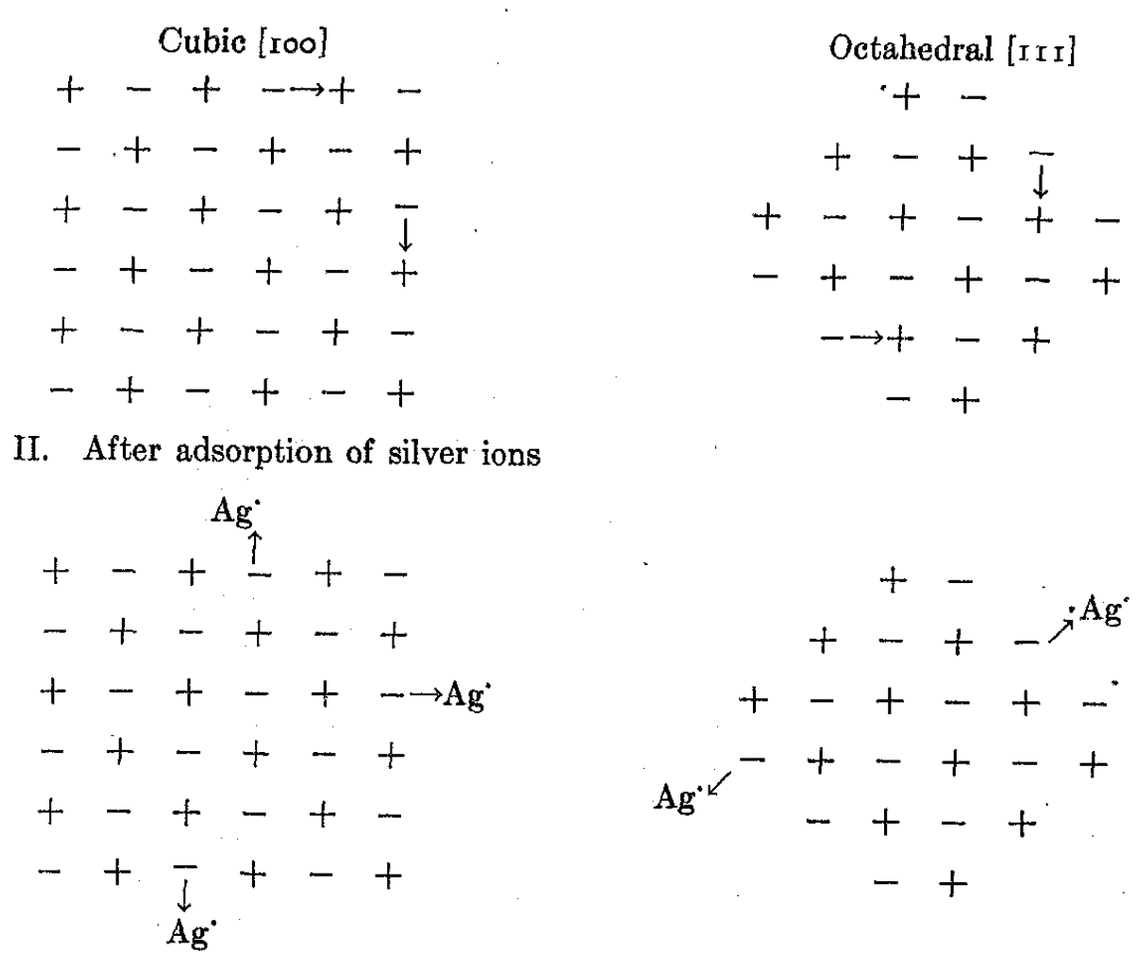
[5] Fajans and Beckerath: Z. physik. Chem., **97**, 478 (1921); Fajans and Frankenburger: **105**, 255 (1923); Fajans and Hassel: Z. Elektrochem., **29**, 499 (1923); Steiner: Z. physik. Chem., **125**,275 (1927).

[6] J. prakt. Chem., **72**, 39 (1905); **73**, 374 (1906); Z. physik. Chem., **60**, 451 (1907); **70**, 239 (1910).

[7] Z. physik. Chem., **105**, 255 (1923).

[8] Cf. Sheppard and Trivelli: Eder, "Ausführliches Handbuch der Photographie, Grundlage des Negativeprozesses," 735 (1926).

[9] Cf. Fajans and Frankenburger: Z. physik. Chem., **105**, 263 (1923).



Now if one represents by an arrow the point at which an electron from a bromine ion is transferred to the neighboring silver ion, an obvious difference is observed, a smaller amount of energy will be required for the electron transfer and hence the liberation of free silver in the presence of adsorbed silver ion than in a normal surface.

Since both zinc and sulfur are obtained by the photochemical decomposition of a sensitive sulfide it would seem that, as in the case of silver bromide, the primary process consists in an exchange of the electrostatic charges of

the ions with the liberation of the free elements. Analogous to the behavior of the silver halide in the presence of adsorbed silver ion, it follows that adsorbed zinc ions will cut down the energy required to decompose zinc sulfide and liberate the atoms of which it is composed. Since a salt always shows a strong tendency to adsorb its own ions, there is little doubt but that zinc ions will be preferentially adsorbed at a zinc sulfide surface, just as ions are adsorbed at a silver halide surface. From this point of view, any factor which favors the formation of zinc ions in the immediate region of the surface of zinc sulfide will tend to increase its sensitivity toward light. As a matter of fact, certain soluble zinc salts have a pronounced sensitizing action whereas insoluble zinc salts have little effect; moreover, ignition in the presence of a small amount of chloride or bromide which form soluble zinc salts, favors the blackening while ignition with fluorides, phosphates, or borates which form insoluble salts, retards or prevents blackening.[1]

From these considerations it follows that the role of water in the photochemical decomposition of zinc sulfide is merely that of an ionizing solvent for the sulfide and for adsorbed zinc salts, yielding zinc ions which are adsorbed on the surface of the sulfide lattice and sensitize it. As has been pointed out, natural zinc blende and precipitated blende are ordinarily light-stable whereas wurtzite is decomposed by ultraviolet light. The difference in behavior is readily understood when one recalls that wurtzite is 4.5 times as soluble as blende.[2] This means not only that the stability of the wurtzite lattice is the smaller but that it yields more readily the zinc ions which play such an important part in the darkening process.

Since a solution of a suitable acid or zinc salt increases the sensitivity of wurtzite enormously, it seemed likely that precipitated zinc sulfide might be made to darken under suitable conditions. This proved to be the case. A twenty percent solution of recrystallized zinc sulfate was treated with ammonia short of precipitation, and a stream of specially purified hydrogen sulfide[3] was passed into the solution very slowly avoiding complete precipitation. In this way, fairly large crystals were formed in the presence of zinc ion. After filtering and washing out the excess sulfate, the sample was placed in a clear quartz test tube, covered with a solution of zinc chloride and exposed to the light from a Cooper-Hewitt lamp running on three amperes direct current. With the test tube 1 centimeter from the lamp distinct blackening was observed in five minutes. If the sample was placed in a test tube of glass instead of quartz, no blackening resulted on prolonged exposure. A sample of blende precipitated slowly from chloride solution was more sensitive than the one thrown down from sulfate. If the sulfide is precipitated rapidly from ammoniacal solution with sodium or ammonium sulfide, a gel is obtained which is not blackened by quartz ultraviolet light in the presence of zinc chloride. Hence it appears that a distinct crystalline structure is essential to light-sensitivity in the sulfide.

[1] See also page 1244.

[2] Gmelin's "Handbuch anorg. Chemie," 8th Ed., **32**, 201 (1924).

[3] Lenz: Z. anal. Chem., **22**, 393 (1883).

Since the preferential adsorption of zinc ion sensitizes the sulfide, it seemed likely that the presence of a salt yielding an anion which is more readily adsorbed than the cation would stabilize the sulfide. Referring once more to the case of silver bromide, it would appear from III, page 1241 that adsorbed bromide ion would tend to stabilize the lattice, since the passage of an electron in the direction of the arrow would be opposed by the electrostatic repulsion of the adsorbed ion. Fajans and Steiner[1] believe that adsorbed bromide ion should sensitize the lattice since it is reasoned that an electron should pass from the adsorbed bromide ion to the silver with a smaller expenditure of energy than from a bromide ion in the lattice. It should be pointed out, however, that the transfer of an electron from the adsorbed ion will be opposed by the electrostatic repulsion of five bromide ions surrounding the silver ion in the surface of the lattice while the passage of an electron from a bromide ion to the silver in a normal surface will be opposed by the electrostatic repulsion of but four ions. It therefore, becomes a question of fact whether the adsorbed bromide ion will sensitize the normal lattice, stabilize the normal lattice, or have no measurable effect. Frankenburger[2] found the spectrum sensitivity threshold to lie between 410 and 435$\mu\mu$ for a slightly acid silver bromide containing adsorbed bromide ion and for a pure dry silver bromide formed by the action of bromine on a silver plate and illuminated in a vacuum. The failure of the adsorbed bromide ion to sensitize the silver salt was attributed by Frankenburger to the desensitizing action of hydrogen ion adsorbed on the adsorbed bromide. Later Steiner[3] found that the sensitivity of a salt with adsorbed bromide was the same in acid and in neutral solution. From these observations one would conclude that the sensitivity of the normal lattice is neither increased nor decreased by adsorbed bromide ion. In some preliminary experiments we have found however that a sample of silver bromide washed repeatedly by the aid of the centrifuge is darkened slightly less rapidly when suspended in silver bromide solution than when suspended in water. This is in line with Wetzlar's[4] observation of a century ago that silver chloride darkens less rapidly in sodium chloride solution than in water.

Although the light-sensitivity of silver bromide is not greatly altered in potassium bromide solution, that of zinc sulfide is decreased enormously in a sodium sulfide solution. Thus a sensitive sulfide covered with water was blackened by two minutes exposure to quartz ultraviolet light while the same preparation covered by a sodium sulfide solution as dilute as N/50 showed no signs of blackening after 30 minutes exposure to quartz ultraviolet light of the same intensity.

The results of a number of observations have been collected together in Table I. Sample I was obtained by treating a zinc sulfate solution with hydrogen sulfide, washing, drying on the water bath and igniting in an electric

[1] Z. physik. Chem., **125**, 307 (1927).
[2] Z. physik. Chem., **105**, 255 (1923).
[3] Z. physik. Chem., **125**, 275 (1927).
[4] Pogg. Ann., **9**, 172 (1827).

tube furnace out of contact with air at 1150° for five hours. Sample 2 was ignited for five minutes at 1150° after mixing with ten percent of KCl to serve as a flux. Samples 3 and 4 were formed by incomplete precipitation with hydrogen sulfide of solutions of $ZnSO_4$ and $ZnCl_2$, respectively, filtered but not washed or ignited. Samples 6 and 7 were gels precipitated from $ZnCl_2$ solution with Na_2S and $(NH_4)_2S$, respectively, washed but not heated. In the table, the designation "no" means no darkening after continuous exposure for 30 minutes to the light of a 3-ampere Cooper-Hewitt mercury lamp at a distance of 1 centimeter. The time designations in the table refer to the time required for a distinct darkening under the above conditions.

TABLE I

Composition of liquid in contact with ZnS	Ultra-violet light through	Action of light on samples					
		1	2	3	4	5	6
Water	glass	no	25 min.	no	no	no	no
N/10 $ZnCl_2$	glass	no	10 min.	no	no	no	no
Water	quartz	10 min.	3 min.	no	no	no	no
N/10 $ZnCl_2$	quartz	5 min.	1 min.	no	no	no	no
N/$ZnCl_2$	quartz	2 min.	1 min.	5 min.	2 min.	no	no
N/50 Na_2S	quartz	no	no	no	no	no	no
N/10 Na_2SO_4	quartz	10 min.	6 min.	no	no	no	no
N/10 $Na_2B_4O_7$	quartz	no	no	no	no	no	no
N/10 Na_2HPO_4	quartz	no	20 min.	no	no	no	no

In accord with the theory outlined above the results tabulated show (1) that a solution of zinc chloride sensitizes the sulfide, causing even the precipitated blende to darken (2) that alkali salts of strongly adsorbed multivalent cations retard or prevent the darkening under the experimental conditions. This observation has been extended to other substances which would seem to be of practical value in preventing the darkening of lithopone paints. Nishizawa[1] found that the sulfide was stabiiized by glycerol, hydroxides, and the salts and esters of tartaric and polyhydroxystearic acids. The stabilization was due to the strongly adsorbed anions of these compounds, but this was not understood by Nishizawa.

The Decolorization Process

Mention has been made of the fact that a blackened sulfide becomes white again in the dark. This process takes place only in the presence of oxygen or some oxidizing agent such as chlorine, ozone, or hydrogen peroxide. It is obvious, therefore, that the process is only partly reversible, if at all, the discoloration in the air being due to the oxidation of the finely divided metal to white zinc oxide or basic carbonate.[2] As already mentioned, Lenard's[3] view is that the photochemical process is reversible. This is based

[1] J. Tokoyo Chem. Soc., **41**, 1054 (1920); Chem. Abstracts, **15**, 1407 (1921); British Pat., 156, 971 (1919).
[2] O'Brien: J. Phys. Chem., **19**, 113 (1915).
[3] Ann. Physik, (4) **68**, 553 (1922).

on his observation that a sulfide thrice darkened and allowed to whiten, appeared to be as sensitive as the original preparation. Apparently, Lenard started out to prove that the reaction is reversible or he would not have been content with three repetitions. Such a small amount of decomposition takes place that the darkening and decolorization must be repeated a number of times before a marked decrease in sensitivity is noted. Phipson reported that his classic gate post, painted with lithopone, became alternately dark in the daytime and black at night for a long time; but at last, it remained white. The permanent white color on prolonged ageing was probably due to a protecting film of oxide or basic carbonate. There was, apparently, no oxidation of the zinc sulfide to zinc sulfate.[1]

Convinced that the photochemical process is reversible, Lenard assumes that discoloration in the presence of oxygen, chlorine, ozone, or hydrogen peroxide is due to the catalytic action of the oxidizing agent on the recombination of zinc and sulfur. This view is absurd, since it is well known that zinc reacts more readily with chlorine or ozone than with sulfur. Lenard recognizes this condition but gets around it by saying that the zinc atoms which cause the darkening are merely "loosened," whereas we know definitely that the blackening is caused by free zinc.

The results of this investigation may be summarized as follows:

1. Zinc sulfide does not undergo photochemical decomposition with quartz ultraviolet light in the absence of water. The water does not serve as a catalyst, as in the case of the thermal decomposition of ammonium chloride; it does not act as a component for the photosynthesis of formaldehyde which would reduce the sulfide (Maass and Kempf); it does not function by being adsorbed on the sulfur atoms of so-called "center molecules" (Lenard). The role of the water is that of an ionizing solvent for zinc sulfide and adsorbed zinc salts yielding zinc ions which are adsorbed on the sulfide lattice rendering it sensitive to the action of light.

2. Soluble zinc salts of univalent anions greately increase the photochemical sensitivity of zinc sulfide. Thus, unignited zinc blende which is ordinarily light-stable, can be prepared so that it will blacken on exposure to quartz ultraviolet light in the presence of zinc chloride.

3. Conversely, salts containing ions which are more readily adsorbed than the cations reduce or prevent the darkening of zinc sulfide by light.

4. The mechanism of photochemical sensitization and stabilization by adsorbed ions is discussed.

Department of Chemistry,
The Rice Institute,
Houston, Texas.

[1] Wolff: Z. angew. Chem., 37, 333 (1924).

THE CREEPING OF SOLUTIONS*

BY E. ROGER WASHBURN

It is not an uncommon experience, in almost every chemical laboratory, to see the glass walls of beakers or crystallizing dishes, above the surfaces of evaporating solutions, lined or coated with a solid deposit of the material which had been in solution. This deposit is usually present on the walls not only throughout the space through which the solution has been lowered by evaporation but often several centimeters above the original level of the solution. In fact the deposit often creeps to the top of the containing vessel and down on the outside, sometimes even spreading out on the table top around the dish.

The progress of a typical experiment will be described in detail. A glass crystallizing dish was filled about one third full of an aqueous solution of sodium chloride. As the water evaporated, crystals of the salt appeared on the surface of the liquid, on the bottom of the dish, and on the sides at the point where the meniscus seems to become parallel to the vertical walls. As the evaporation continued, the deposit seemed to creep up the walls, over the top, and down on the outside. The solid deposit reached a thickness of almost a centimeter at the top of the dish. Soon some of the solution started to spread out on the table around the dish, in much the same manner that it would have done if the bottom of the dish had been cracked. The bottom was, however, perfectly intact.

The aqueous solutions of a number of the readily soluble salts have been studied in this connection. Among others, there might be mentioned, barium chloride, sodium nitrate, potassium nitrate, copper sulphate and potassium dichromate. Each of these solutions showed the same tendency to creep on the glass walls, copper sulphate showing the phenomenon to an especially marked degree.

Solutions in other solvents than water have also been found to display the same tendency to creep up the sides of dishes. Naphthalene in such solvents as ethyl alcohol, benzene and toluene shows a tendency to creep under ordinary laboratory conditions. Sulfur in carbon disulfide displays the phenomenon in a manner easily studied because of the rapid evaporation of the solvent.

That solutions will climb on other materials than glass is to be expected and is of interest. Although it seems to be difficult to clean the surfaces of some metals or to prevent reactions between them and the concentrated salt solutions, it has been observed that the solutions of such salts as have been mentioned will creep on gold, silver and platinum. The creeping also takes place on porcelain. Sulfur in carbon disulfide shows a marked tendency to climb on copper. The fact that the copper becomes coated with a thin layer of black copper sulfide immediately upon being immersed in the solution does not prevent the climbing.

* Contribution from the Chemistry Laboratory of the University of Nebraska.

This phenomenon is so common that few stop to wonder at it, or to seek an explanation. In fact a search of the literature failed to bring to light any reference to the subject or its causes. The results of a number of experiments have led to the following interpretation. The nature of the observations have been such that results of a quantitative nature cannot be presented, although it may be that certain phases of the problem do deserve a more quantitative study.

When an evaporating solution wets the walls with which it is in contact it will rise on them above the body of the liquid. As evaporation takes place crystallization will set in, usually at the surface, both on the body of the solution and on the film on the walls. The crystals on the surface of the film form a more or less compact crust at the point of first formation. This crust conforms to, but is not in actual contact with, the supporting walls. There is thus formed a capillary space bounded on one side by the crystal crust and on the other by the wall material. Solution rises through this capillary layer, wetting the walls and thus climbing to a new height; the crust grows, perhaps to each side as well as upward, and more liquid rises in its self-made capillary. In cases where a solid crust is not formed there are also capillary layers between the crystals through which liquid may climb. We have been led to believe, however, that the greater part of the liquid rises through the capillary between the crust and the walls.

Experimental facts which have led to this explanation may be summed up as follows.

If the solution does not wet the walls, the crust does not form above the liquid level, and the solution does not climb noticeably on the walls. For example, solutions of salts do not climb in vessels coated with paraffin. The climbing does not occur if the walls are oily or greasy. The climbing of a solution, which may have started on clean walls, may be stopped by painting on the walls above the solution with hot paraffin. The crust will form up to the paraffin layer and stop, conforming in outline to the painted stripe.

When evaporation is slow, or is prevented, little or no crust will form and grow. Saturated solution of salts, or of sulfur in carbon disulfide, do not form crusts in stoppered bottles. If a clean test tube be inverted into the evaporating solution of some salt the crust will form and the solution will climb on the outside but not on the inside of the tube. If the bottom be punched out of the tube, however, and a gentle current of air be blown in and out, the crust will form and the solution will climb on the inside.

If the crust of crystals above the solution be gently pressed aside it will be observed that the crystals are separated from the glass by a liquid layer. The moisture can be seen or otherwise tested for, and the fact that the crust is loose from the solid wall is evident by the ease with which it is moved. After sufficient time has elapsed for the liquid to evaporate entirely from the capillary layer, the crust will crumble easily if it is thick; but it may adhere to the glass walls with considerable force if it is thin.

That the solution must climb through a self-made capillary is indicated by the following simple experiment. A saturated solution of sulfur in carbon

disulfide was placed in a small bottle to the depth of about one centimeter. The walls above the solution were oily so that they were not wet by the solution. A narrow strip of copper was then placed in the bottle, with the bottom in the solution and the top resting against one side at the top of the bottle. The solution wet the metal and the crust soon began to form and to climb until it reached the top of the strip. No climbing was observed on the glass just above the solution. When the solution of sulfur reached the top of the bottle on the copper strip it spread out on the glass which here was clean, completely covering the upper portion before the liquid in the bottle had all evaporated. Experiments of this type require several hours for completion, which would indicate that the solution must be well protected from evaporation until it reaches the top for, as is well known, carbon disulfide evaporates very rapidly.

In very favorable, and therefore rather uncommon, instances the crust climbs up and over the top of the walls and down on the outside far enough so that it will actually siphon the remaining liquid out of the dish through the capillary layer. This phenomenon is similar to the siphoning of a liquid out of a dish through a wick or other porous fabric. Of course, when the crust is once over the top of the wall, surface tension or wetting ceases to be the principal factor in causing the downward spread for the force of gravity readily accounts for the further growth.

Attention should be called to the interesting and somewhat similar experiment mentioned by W. D. Bancroft,[1] in connection with the apparently coherent layer of metal which rises in the liquid film several centimeters above the level of the liquid in which one has shaken aluminum powder or copper powder. Although this phenomenon is different from the one which has been described in that evaporation is not an essential factor it is pertinent because it offers additional evidence that a liquid film may rise some distance on the walls above the main level of the liquid. The same phenomenon is shown by the tendency of very fine precipitates, such as barium sulfate, to creep up in the liquid layer on the walls of beakers above the solution and thus sometimes cause trouble in analytical work.

It is doubtful whether any important information may be obtained by a quantitative study of the relative amounts of climbing on different surfaces for the following reasons. If the liquid does not wet the surface at all, it will not climb at all. If it does wet it, even a little; in other words if attraction or adhesion between the liquid and the solid is greater than the cohesional forces of the liquid, the liquid will climb and on evaporating will build its capillary through which it will rise a little higher. This process will continue until a height is reached, the same for all clean, wetted, surfaces, determined only by the surface tension of the solution and the diameter of the capillary space through which it climbs; providing that the capillary layers do not become blocked by crystals growing together and in actual contact with the glass.

[1] "Applied Colloid Chemistry," pp. 104-105 (1926).

26

THERMODYNAMIC POSSIBILITIES OF THE SILVER SULFIDE BROMINE-ACCEPTOR HYPOTHESIS OF LATENT IMAGE FORMATION*

BY R. H. LAMBERT AND E. P. WIGHTMAN**

Introduction

The sensitivity substance present in the gelatin of high-speed photographic emulsions has been traced by Sheppard to organic compounds containing sulfur, which react under certain conditions with silver halide to form silver sulfide.[1, 2] Such silver sulfide appears to be concentrated in minute specks on or imbedded in the surface of the halide grains.[3, 4] The sensitizing action of these centers has become the subject of some interesting speculation. Those interested are referred to the papers of Sheppard and co-workers on the hypothesis of orientation and crystal strain, [1, 2, 5] and to the earlier work of others before the nature of the specks was known.†

Recently a new conception of the role of the speck in sensitivity was advanced by Hickman.[6] He proposed that silver sulfide acts as a halogen-acceptor, and in so doing, that it also becomes the agent for the deposition of more metallic silver than would ordinarily be produced simply by the action of light on silver halide. In other words, he proposes a chemical theory which may either supplement, or even replace the orientation-strain theory.

The mechanism of Hickman's hypothesis is essentially as follows. When light acts on silver bromide, the bromine set free, at first in the atomic condition, probably attacks the silver sulfide speck or other halogen-acceptor before it has had a chance to become molecular, since it is liberated at the interface between the solid silver halide and the sensitivity speck. Two possible alternative series of reactions are suggested as the result of this attack:

Series (1) is regarded by him as the more probable since under light action it is unlikely that silver bromide would again be formed even by way of sulfide attack.

As opposed to the idea of sulfur being formed, Renwick,[7] in a criticism of Hickman's paper, points out that sulfur actually acts as a desensitizer. We shall not attempt to deal with this criticism, but will have something more to say presently as to the probability of the above series of reactions.

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[1] S. E. Sheppard: Colloid Symposium Monograph, **3**, 76 (1925).

[2] S. E. Sheppard: Phot. J., **65**, 380 (1925); **66**, 505 (1926).

[3] S. E. Sheppard and H. Hudson: Paper to be published shortly.

[4] S. E. Sheppard, A. P. H. Trivelli and E. P. Wightman: Paper in press. Reference is made here to previous work, including that of Svedberg, Toy, and others, on the existence of sensitivity specks.

[5] S. E. Sheppard, A. P. H. Trivelli, and R. Loveland: J. Franklin Inst., **200**, 51 (1925).

† Referred to in the above-mentioned papers of Sheppard and co-workers.

[6] K. C. D. Hickman: Phot. J., **67**, 34 (1927).

[7] F. F. Renwick: Phot. J., **67**, 41 (1927).

SERIES 1

$$2\ AgBr \downarrow + 2E$$
$$2\ Ag + 2\ Br \downarrow + 2\ Ag_2S$$
$$4\ Ag + S_2Br_2 \downarrow + 8\ H_2O$$
$$10H + 2\ H_2SO_4 + 2HBr \downarrow + 10\ AgBr$$
$$\underline{10\ Ag} + 10\ HBr$$

TOTAL = 16 Ag metal

SERIES 2

$$2\ AgBr \downarrow + 2E$$
$$2\ Ag + 2\ Br \downarrow + Ag_2S$$
$$2\ AgBr + S \downarrow + 4\ H_2O$$
$$6H + H_2SO_4 \downarrow + 6AgBr$$
$$\underline{6\ Ag} + 6\ HBr$$

TOTAL = 8 Ag metal

It is not claimed by Hickman that these particular chain reactions are the ones involved; he regards the above formulations as only symbolical. However, he gives experimental evidence which indicates that the sulfide does act as an acceptor, and moreover, that a greater amount of silver is formed than would be expected from the photochemical decomposition of the silver halide.

He finds that a photographic film or paper treated with a soluble sulfide and then exposed to light until a strong print-out image forms, gives a greater visual photo-product than one untreated. He shows further that this is not caused by light decomposition of the sulfide, but that the sulfided portion is bleached by the light action. This, he concludes, is due to the action of the bromine set free by the photochemical decomposition of the surrounding silver bromide.

Since a decrease of free energy indicates the possibility of a reaction proceeding, and since in some cases at least the magnitude of the decrease is a measure of the tendency of the reaction to occur, we have calculated the free energy changes of the above reactions and also of some other suggested procedures in order to find out whether or not any of them are possible, and if *possible* which would be the more likely to occur.

Free Energy Data

Free energies of formation of substances involved. Most of the free energy of formation data which we have used have been taken from *Thermodynamics* by Lewis and Randall.[8] These as well as some others to be discussed are summarized in Table I.

Free energy of formation of S_2Br_2 and S_2I_2. Very little data could be found from which free energies could be calculated for sulfur bromide and iodide. Spring and Lacranier state[9] that at equilibrium at room temperature, in a mixture of the compound with its components, sulfur bromide is 27% dissociated and sulfur iodide 90%.

[8] G. N. Lewis and Merle Randall: "Thermodynamics and Free Energies of Chemical Substances," (1923).

[9] W. Spring and A. Lacranier: Bull., 45, 867 (1886).

TABLE I

Free Energies of Formation

Substance	ΔF_{298} in cal.	Substance	ΔF_{298} in cal.
H_2(g)	0*	$S_{8\ \text{rhombic}}$ (s)	0*
H (g)	37,730*	$S_{\lambda,\mu}$ (l)	93*
H_2O (l)	−56,560*	S (g)	30,240*
HBr (Aq)	−24,595*	S_2 (g)	18,280*
HBrO (Aq)	−19,680*	S_2Br_2 (l)	−3,040**
HI (Aq)	−12,361*	S_2I_2 (l)	4,316**
Br_2 (l)	0*	H_2S (Aq)	−6,490*
Br_2 (g)	755*	H_2SO_3 (Aq)	−126,330*
Br (g)	18,250*	H_2SO_4 (Aq)	−176,500*
Br_2 (Aq)	977*	AgBr (s)	−23,730 †
I (s)	0*	AgI (s)	−15,767†
I (g)	15,470*	Ag_2S (s)	−6,355††
I_2 (Aq)	3,926*	Nϵ	76,900

*Lewis and Randall, cf. ref. 8.
**Calcd. from dissociation values of Spring and Lacranier, cf. ref. 9.
†T. J. Webb, cf. ref. 11.
††calcd. from data given by Noyes and Freed, cf. ref. 13.
Calcd. from photochem. equivalence, ie., one mol-quantum of light energy.

In the reaction

$$S_a + 1/2aBr_2 \leftrightarrows 1/2aS_2Br_2 \qquad (1)$$

all the substances are liquid. Lewis and Randall[8] consider liquid sulfur at 25° to consist usually of an equilibrium mixture of S_8 and S_6 which they designate as $S_{\lambda,\mu}$ Since according to them there is only about 0.8% S_μ, i.e., S_6, in the mixture we may neglect it and consider a = 8. So we obtain for the formation constant of reaction (4) the value 198.

$$\text{Since } \Delta F = -R\,T \ln k \qquad (2)$$

where k is the formation constant, and R and T have their usual significance, the value of ΔF can easily be calculated. For S_2Br_2, $\Delta F_{298} = -3{,}133$ cal; and for S_2I_2, $\Delta F_{298} = 5143$ cal., the elements being in the liquid state.

The free energy of transfer of $S_{\lambda,\mu}$ to $S_{(\text{rhombic})}$ is given by Lewis and Randall as $\Delta F_{298} = 93$ cal. Hence, the free energy of formation of S_2Br_2 from liquid bromine and solid sulfur at 25°C is −3,040 cal.

Since the free energy of transfer of liquid to solid iodine is, according to the same authors, −920 cal., the free energy of formation of S_2I_2 from the solid elements is 4,316 cal.

Ogier[10] obtained −2,000 cal. and 0 cal. respectively for the heats of formation of sulfur bromide and iodide; therefore, it may be assumed that the free energy of formation of the bromide as calculated above is not greatly in error. The value for the iodide, however, seems rather high. But, in the absence of any more reliable data we shall have to accept it.

[8] p. 525.
[10] Ogier: Compt. rend., 92, 923 (1881).

As a matter of fact, were the value for the bromide fifty, even a hundred per cent, in error it would not, as will be seen later, alter seriously the final results and conclusions at which we have arrived.

Free energy of formation of AgBr and AgI. The free energy values for silver bromide and iodide are given by T. J. Webb.[11] The value for the former was calculated by him from the data of Lewis and Storch[12] and Lewis and Randall.[8] That of the latter is a very reliable one which he obtained by averaging five independent values very closely in agreement. Both values are given in Table I.

Free energy of formation of Ag_2S. Noyes and Freed[13] determined the electromotive force of the hydrogen-silver sulfide and hydrogen-silver iodide cells. From these the free energy of formation of silver sulfide can be calculated. This value turns out to be -6355 cal.

Solubility and specific heat data, which are available, can also be used to calculate the free energies, but the value so obtained is much less reliable than that given above.

Free energy of 1 mol-quantum of light. Finally, we shall consider the energy of light producing photochemical decomposition of the silver halides.

The energy for one quantum of light is given by the equation

$$\epsilon = hc/\lambda$$

in which h is Planck's constant, 6.547×10^{-27} erg sec.; c is the velocity of light, 2.999×10^{10} cm./sec.; and λ is the wave-length of light. Choosing $\lambda = 370$ mμ, a wave-length to which both silver bromide and iodide are highly sensitive under ordinary conditions, then $\epsilon = 5.307 \times 10^{-12}$ erg or 1.268×10^{-19} cal.

If we assume, as Hickman has done, that one molecule of silver halide (i.e., 1/4 of a crystal molecule according to Bragg) requires one light quantum for decomposition, N would be the energy necessary to decompose one gram-mol, where N is Avogardo's number, 6.062×10^{23}. N is then 76,903 cals. or, in round numbers, 76,900 cal.

Free Energy Change in Various Reactions

The photochemical decomposition of the silver halides. In determining the free energy change in the photochemical decomposition of silver bromide or iodide, two important assumptions had to be made. First, that at least one AgBr pair in the silver bromide lattice—and the same is true for the iodide—is decomposed for each quantum of light energy absorbed, as claimed by Eggert and Noddack,[14] and secondly, that the photochemical energy can supply the free energy of decomposition in the case of a light sensitive substance like silver bromide.

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[11] T. J. Webb: J. Phys. Chem., **29**, 816 (1925).

[12] G. N. Lewis and H. Storch: J. Am. Chem. Soc., **39**, 2544 (1917).

[13] A. A. Noyes and E. S. Freed: J. Am. Chem. Soc., **42**, 476 (1920).

[14] J. Eggert and W. Noddack: Sitzungsber. preuss. Akad. Wiss., **39**, 631 (1921); **41**, 116 (1923); W. Nernst and W. Noddack: **41**, 110 (1923).

Granting these assumptions, we then get

$$AgBr(s) + N\epsilon_{370} = Ag(s) + Br(g); \qquad \Delta F_{298} = -\ 34{,}920 \text{ cal.} \qquad (4)$$

$$_2AgBr(s) + {}_2N\epsilon_{370} = {}_2Ag(s) + Br_2(l); \qquad \Delta F_{298} = -106{,}330 \text{ cal.} \qquad (5)$$

depending upon whether we have the formation of gaseous atomic or liquid molecular bromine.

The corresponding reactions for silver iodide are

$$AgI(s) + N\epsilon_{370} = Ag(s) + I(g); \qquad \Delta F_{298} = -\ 45{,}663 \text{ cal.} \qquad (6)$$

$$_2AgI(s) + {}_2N\epsilon_{370} = {}_2Ag(s) + I_2(s); \qquad \Delta F_{298} = -122{,}266 \text{ cal.} \qquad (7)$$

It appears from this that silver iodide should be more sensitive to light than silver bromide. This is known to be true, but the relative developability in ordinary developers is in the reverse direction.

If it is assumed that bromine or iodine when set free goes immediately into solution in the water in the emulsion—present usually to the extent of 5 to 10% by weight of the dry emulsion—before it can be taken up by an acceptor, the free energy decrease of the reaction corresponding to equation (4) would be −52,682 cal. This assumption, however, seems rather improbable when a halogen-acceptor like silver sulfide is in immediate contact with the silver halide lattice.

The Ag_2S—bromine-acceptor reactions. We are now prepared to test Hickman's and other series of reactions or postulates:

Postulate 1, via S_2Br_2

$$_2AgBr(s) + {}_2N\epsilon = {}_2Ag(s) + {}_2Br(g); \qquad \Delta F_{298} = -\ 69{,}840 \text{ cal.} \quad (a)$$

$$_2Ag_2S(s) + {}_2Br(g) = {}_4Ag(s) + S_2Br_2(l); \qquad \Delta F_{298} = -\ 26{,}830 \text{ cal.} \quad (b)$$

$$S_2Br_2(l) + 8H_2O(l) = {}_2HBr(Aq) + {}_2H_2SO_4(Aq) + {}_{10}H(g); \qquad \Delta F_{298} = +430{,}630 \text{ cal.} \quad (c)$$

$$_{10}H(g) + {}_{10}AgBr(s) = {}_{10}Ag(s) + {}_{10}HBr(Aq); \qquad \Delta F_{298} = -385{,}950 \text{ cal.} \quad (d)$$

Adding these four equations and dividing by 2:

$$6AgBr(s) + Ag_2S(s) + 4H_2O(l) + N\epsilon = H_2SO_4(Aq) + 6HBr(Aq) + 8Ag(s); \qquad \Delta F_{298} = -\ 25{,}995 \text{ cal.} \qquad (8)$$

Postulate 2, via $S_{(atomic)}$

$$_2AgBr(s) + {}_2N\epsilon = {}_2Ag(s) + {}_2Br(g); \qquad \Delta F_{298} = -\ 69{,}840 \text{ cal.} \quad (a)$$

$$Ag_2S(s) + {}_2Br(g) = {}_2AgBr(s) + S(g); \qquad \Delta F_{298} = -\ 47{,}365 \text{ cal.} \quad (b)$$

$$S(g) + 4H_2O(l) = H_2SO_4(Aq) + 6H(g); \qquad \Delta F_{298} = +245{,}880 \text{ cal.} \quad (c)$$

$$6H(g) + 6AgBr(s) = 6Ag(s) + 6HBr(Aq); \qquad \Delta F_{298} = -231{,}570 \text{ cal.} \quad (d)$$

$$6AgBr(s) + Ag_2S(s) + 4H_2O(l) + {}_2N\epsilon = H_2SO_4(Aq) + 6HBr(Aq) + 8Ag(s); \qquad \Delta F_{298} = -102{,}985 \text{ cal.} \qquad (9)$$

First of all, it is seen that in Postulates 1 and 2 of Hickman that reaction (c) in each case gives an enormous positive free energy, even greater than the sum of the negative free energies of the first two reactions. It appears unlikely then that the latent image formation could follow such a procedure. Even if the atomic hydrogen in each case were to form molecular hydrogen

first, before acting on the silver halide, the free energy would still be positive, +53,330 cal. in Postulate 1 and +19,600 cal. in Postulate 2. We discuss this matter more fully below.

Hickman was careful to state that he did not limit himself to these two series of reactions but he did not mention any other specific ones, except to say that the oxidation might not proceed to sulfuric acid but might stop short at sulfurous acid. Even this does not give a negative free energy. Slater Price,[15] in a criticism of Hickman's hypothesis, mentioned the fact that bromine reacts with water to give hypobromous acid. On the basis of this suggestion we have Postulate 3.

Postulate 3, via HBrO

$$8AgBr(s) + 8\,N\epsilon = 8Ag(s) + 8Br(g); \qquad \Delta F_{298} = -279{,}360 \text{ cal.} \quad (a)$$

$$8Br(g) + 4H_2O(l) = 4HBr(Aq) + 4HBrO(Aq); \qquad \Delta F_{298} = -96{,}860 \text{ cal.} \quad (b)$$

$$Ag_2S(s) + 4HBrO(Aq) = 2AgBr(s) + 2HBr(Aq) + H_2SO_4(Aq); \qquad \Delta F_{298} = -188{,}075 \text{ cal.} \quad (c)$$

$$6AgBr(s) + Ag_2S(s) + 4H_2O(l) + 8\,N\epsilon = H_2SO_4(Aq) + 6HBr(Aq) + 8Ag(s); \qquad \Delta F_{298} = -564{,}295 \text{ cal.} \quad (10)$$

Here, since all the intermediate reactions show a decrease in free energy, the process appears thermodynamically possible. It is to be noted, however, that no silver results except by the photochemical decomposition, which has to be considerable in order to furnish sufficient bromine for the reaction to proceed. In other words, only large exposures would be expected to produce this result. In this case, the moisture in the plate serves as the bromine absorber and the silver sulfide acts only indirectly. There are other modifications of this procedure of course. For instance, it is unlikely that so much bromine would be formed at once and remain in the atomic condition before acting. This would cause reaction (b) to have a positive free energy, thus

Postulate 3A, via HBrO and liquid Br

$$8AgBr(s) + 8\,N\epsilon = 8Ag(s) + 4Br_2(l); \qquad \Delta F_{298} = -425{,}360 \text{ cal.} \quad (a)$$

$$4Br_2(l) + 4H_2O(l) = 4HBr(Aq) + 4HBrO(Aq); \qquad \Delta F_{298} = +49{,}140 \text{ cal.} \quad (b)$$

Since reaction (b) in Postulates 1 and 2 are both possible, let us consider if we can find some other way in which the sulfur bromide or the sulfur may react with the water or silver bromide, the most likely things for them to act upon.

We have not found any statements in the literature as to just how sulfur bromide acts with water, although we know it does. The following postulate suggests itself (Postulate 4).

[15] T. Slater Price: Phot. J., 67, 40 (1927).

Postulate 4, via S_2Br_2 and H_2S

$2AgBr(s) + 2N\epsilon = 2Ag(s) + 2Br(g)$; $\triangle F_{298} = -69{,}840$ cal. (a)

$2Ag_2S(s) + 2Br(g) = 4Ag(s) + S_2Br_2(l)$; $\triangle F_{298} = -26{,}830$ cal. (b)

$S_2Br_2(l) + 3H_2O(l) = H_2S(Aq) + H_2SO_3(Aq) + 2HBr(Aq)$; $\triangle F_{298} = -9{,}290$ cal. (c)

$H_2S(Aq) + 2AgBr(s) = Ag_2S + 2HBr(Aq)$; $\triangle F_{298} = -1{,}595$ cal. (d)

$4AgBr(s) + Ag_2S(s) + 3H_2O(l) + 2N\epsilon = H_2SO_3(Aq) + 4HBr(Aq) + 6Ag(s)$; $\triangle F_{298} = -107{,}555$ cal. (6)

and similarly where S is first formed:

Postulate 5, via S and S_2Br_2

$6AgBr(s) + 6N\epsilon = 6Ag(s) + 3Br_2(l)$; $\triangle F_{298} = -319{,}020$ cal. (a)

$2Ag_2S(s) + 2Br_2(l) = 4AgBr(s) + S_2(g)$; $\triangle F_{298} = -63{,}930$ cal. (b)

$S_2(g) + Br_2(l) = S_2Br_2(l)$; $\triangle F_{298} = -21{,}320$ cal. (c)

$S_2Br_2(l) + 3H_2O(l) = H_2S(Aq) + H_2SO_3(Aq) + 2HBr(Aq)$; $\triangle F_{298} = -9{,}290$ cal. (d)

$H_2S(Aq) + 2AgBr(s) = Ag_2S(s) + 2HBr(Aq)$ $\triangle F_{298} = -1{,}595$ cal. (e)

$4AgBr(s) + Ag_2S(s) + 3H_2O(l) + 6N\epsilon = H_2SO_3(Aq) + 4HBr(Aq) + 6Ag(s)$; $\triangle F_{298} = -415{,}155$ cal. (11)

In an atmosphere of oxygen the sulfurous acid formed would likely soon be oxidized to sulfuric acid, thus:

$2H_2SO_3(Aq) + O_2(g) = 2H_2SO_4(Aq)$; $\triangle F_{298} = -100{,}340$ cal. (f)

Hickman is of the opinion that, even in a chain reaction such as postulate 4 or 5, H_2S cannot form even if only instantaneously in the presence of H_2SO_3 but that free sulfur would be formed. If this were true, then we should have one of the two following.

$2S_2Br_2(l) + 3H_2O(l) = 3S(g) + 4HBr(Aq) + H_2SO_3(Aq)$; $\triangle F = +41{,}770$ cal. (c′)

$2S_2Br_2(l) + 3H_2O(l) = 3/8\ S_8$ (rhombic)(s) $+ 4HBr(Aq) + H_2SO_3(Aq)$; $\triangle F = -48{,}950$ cal. (c″)

Reaction (c′) gives a positive free energy and is therefore unlikely and (c″) seems improbable unless sufficient S_2Br_2 were formed to give a whole instead of a fractional molecule of sulfur.

The action of atomic sulfur on water we have already considered. There are also some other possibilities which we shall not attempt to give here.

Notice that in the case of Postulate 4, 4 atoms of silver are produced from 2 silver sulfide, but none from silver bromide except that due to light action, some silver sulfide being regenerated. All the intermediate reactions show a free energy decrease.

In Postulate 5, which is a variation of 2, we again have a decrease of free energy throughout, but only silver due to light action is produced.

So far, we have been unable to find any series of intermediate reactions which would produce silver aside from that caused by the photochemical decomposition itself, except as in Postulate 4, and as noted below. The fact that all the intermediate reactions in Postulates 3, 4, and 5 show a fairly large

negative free energy would indicate that they are admissible thermodynamically, and hence, that these postulates are more plausible than Postulates 1 and 2.

To be sure, if molecular hydrogen were to be formed instantly in Postulate 2 reaction (c), and if sulfurous instead of sulfuric acid were formed, the energy supplied by the photochemical decomposition of AgBr and by the formation of S_2Br_2 or of S would be greater in each case than that of reaction (c), (the oxidation of the S_2Br_2 or S) and the sum of free energies of the first two reactions might be sufficient to force reaction (c) to take place, especially when the hydrogen so formed would be instantaneously disposed of according to reaction (d), (the reduction of silver bromide)..

Postulate 6, via S_2Br_2 and H_2SO_3

$2AgBr(s) + 2N\epsilon$	$2Ag(s) + 2Br(g)$;	$\triangle F_{298} = -69{,}840$ cal.	(a)
$2Ag_2S(s) + 2Br(g)$	$= 4Ag(s) + S_2Br_2(l)$;	$\triangle F_{298} = -26{,}830$ cal.	(b)
$S_2Br_2(l) + 6H_2O(l)$	$= 2HBr(Aq) + 2H_2SO_3$ (Aq)		
	$+ 3H_2(g)$;	$\triangle F_{298} = +41{,}550$ cal.	(c)
$3H_2(g) + 6AgBr(s)$	$= 6Ag(s) + 6HBr(Aq)$;	$\triangle F_{298} = -5{,}190$ cal.	(d)
$8AgBr(s) + 2Ag_2S(s) + 6H_2O + 2N\epsilon =$			
$H_2SO_3(Aq) + 6HBr(Aq) + 12Ag(s)$;		$\triangle F_{298} = -60{,}310$ cal.	(12)

Postulate 7, via S (atomic) and H_2SO_3

$2AgBr(s) + 2N\epsilon$	$= 2Ag(s) + 2Br(g)$;	$\triangle F_{298} = -69{,}840$ cal.	(a)
$Ag_2S(s) + 2Br(g)$	$= 2AgBr + S(g)$;	$\triangle F_{298} = -47{,}365$ cal.	(b)
$S(g) + 3H_2O(l)$	$= H_2SO_3(Aq) + 2H_2(g)$;	$\triangle F_{298} = +13{,}110$ cal.	(c)
$2H_2(g) + 4AgBr(s)$	$= 4Ag(s) + 4HBr(Aq)$;	$\triangle F_{298} = -3{,}460$ cal.	(d)
$6AgBr(s) + Ag_2S(s) + 3H_2O(l) + 2N\epsilon =$			
$H_2SO_3(Aq) + 4HBr(Aq) + 6Ag(s)$;		$\triangle F_{298} = -107{,}555$ cal.	(13)

There is one way suggested to us by Hickman by which silver might be formed from silver bromide aside from the photochemical decomposition. This is by oxidizing sulfurous to sulfuric acid.

Reduction of AgBr by $H_2SO_3(Aq)$

$H_2SO_3(Aq) + H_2O(l)$	$= H_2SO_4(Aq) + H_2(g)$;	$\triangle F_{298} = +6{,}390$ cal.	(a)
$H_2(g) + 2AgBr(s)$	$= Ag + 2HBr(Aq)$;	$\triangle F_{298} = -1{,}730$ cal.	(b)

If the molecular sulfurous acid has a chance to become ionized we get instead of (a) $2H^+ + 2SO_3^{--} + H_2O(l) = 2H^+ + 2SO_4^{--} +$

$H_2(g)$; $\triangle F_{298} = -3{,}260$ cal. (a′)

The positive free energy of (a) is not large and might easily be overbalanced by the energy set free in the preceeding intermediate reactions.

We might liken this effect, which applies also to the formation of H in Postulates 6 and 7, to that of falling water. In A, Fig. 1 the water always falls from one step to the next.

In B it would fall the first two steps, but would probably not come back over the third step until the depression had been filled because it would have to rise too far, but in C the rise in the third step would slow it down and lessen

its force but would not stop it from falling the remainder of its journey. If the hump in B were higher than the source, no water would fall and in the same way with the series of reactions, nothing would happen.

It must be remembered that in the formation of the latent image the quantities of substances reacting are of the order of a few molecules at the most, and it may be that thermodynamic relationships which have been worked out on the molar basis where millions of molecules are involved are somewhat different from the former. Any statement concerning the possibility or impossibility of a reaction proceeding must therefore be very guarded.

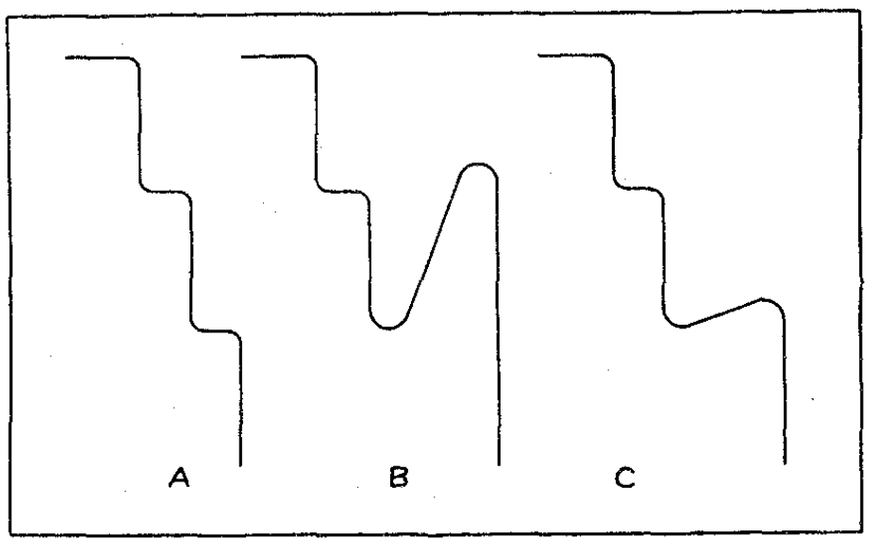


FIG. 1

It should be noted that Hickman found that silver sulfide formed in a photographic emulsion is bleached by the action of light, and silver was formed greater in amount than that produced on an unsulfided portion of the emulsion. This could easily be explained by such a procedure as that in Postulate 4 in which sulfur bromide was formed from the silver sulfide and this was disposed of through reactions, all of which showed free energy decreases.

There is one suggestion which we offer which seems reasonable at first sight, since it appears quite possible thermodynamically. This is that light acts on silver sulfide as well as on the silver bromide; Sheppard has already pointed out[1] that Ag_2S has an electron affinity less than AgBr. In this case we should get something like the following,

$$2Ag_2S(s) + 2N\epsilon = 4Ag(s) + 2S(g); \quad \Delta F_{298} = -80{,}620 \text{ cal.} \quad (a)$$

$$2AgBr(s) + 2S(g) = 2Ag(s) + S_2Br_2(l); \quad \Delta F_{298} = -16{,}006 \text{ cal.} \quad (b)$$

and the S_2Br_2 could react as in one of the preceding postulates. Here, considerable Ag_2S and AgBr are both destroyed and silver is produced to an even greater extent than where AgBr is the photoactive substance.

The objection to this is that the spectral distribution of the light energy in latent image formation appears to be definitely that due to absorption by silver bromide. The spectral distribution in the blue violet remains the same

for sensitized and desensitized plates, and Toy and Edgerton found[16] that the number of centers formed per grain was proportional to the light-absorption by silver bromide at that wave-length. The only possibility of meeting this objection would be to suppose that the silver bromide is acting as an *optical* sensitizer[1] for the *silver sulfide* at the same time that the latter is a chemical sensitizer for the silver bromide.

Summary and Conclusions

It would appear from the data which we have given that Hickman's hypothesis that the silver sulfide can serve as a halogen acceptor in the formation of photographic latent image is sound thermodynamically. The two specific reactions which he proposes tentatively as the mechanism by which to arrive at the latent image, while in their summation showing free energy decreases, contain in each case a reaction with a positive free energy higher than the sum of the free energies of the preceeding reactions.

This throws doubt on the particular intermediate reactions in question, but does not invalidate the hypothesis as a whole. In other words, whatever the route by which we arrive at the final result, it, the final result, appears to be thermodynamically admissible. Following the absorption of the bromine by the silver sulfide, there are numerous series of reactions which may lead to a final equilibrium condition. One of Hickman's fundamental assumptions is that more silver is formed than the photochemical decomposition alone would account for. Most of the reactions which have been investigated do not give rise to more silver than that produced by the photochemical decomposition or from the sulfide by the absorption of the bromine. However, Hickman has suggested to us the reduction of the silver bromide by the sulfurous acid formed. This appears thermodynamically feasible if the surplus energy of the preceeding reactions is taken into account.

Finally, it is suggested that silver sulfide itself in the presence of silver bromide is photochemically decomposed, the silver bromide in this case serving probably as an optical sensitizer of the sulfide, as Sheppard has previously suggested, and as the sulfur acceptor giving rise to sulfur bromide and silver. In this case, much more silver would result than otherwise. The free energy of formation of silver sulfide and of sulfur bromide have been calculated, the one from the electrochemical data of Noyes and Freed, and the other from the work of Spring and Lacranier on the dissociation of sulfur bromide. These are respectively $-6{,}355$ and $-3{,}040$ calories.

Rochester, New York
May 5, 1927.

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[16] F. C. Toy and J. A. Edgerton: Phil. Mag., **48**, 947 (1924).

5-369

RELATION BETWEEN THE METABOLISM OF GLUCOSE AND FATS IN DIABETES

BY N. R. DHAR

In reviewing "An introduction to organic chemistry by Lowy and Harrow," Professor Bancroft[1] has quoted the following lines: "In diabetes, the poisonous acetone or acid bodies, which are so often produced, are derived from fats. These acetone bodies include butyric acid, β-hydroxybutyric acid, acetoacetic acid, and acetone. The acetone is a by-product obtained probably from acetoacetic acid by the loss of CO_2. It would seem as if the diabetic has not only difficulty in oxidizing glucose, but also in completely oxidizing fats; the fats in his case are oxidized to four carbon stage and no farther."

This view of the metabolism in diabetes is also accepted by medical men in general.

In previous papers,[2] I have discussed the problem of metabolism in different forms of diabetes and glycosuria and I have emphasised that vitamin A or thyroid secretion acts as a promoter in the oxidation of fatty food materials and vitamin B or pancreatic secretion behaves as a promoter in the oxidation of carbohydrates.

In this paper I shall try to show that glucose must be oxidized in the body in order to prevent the formation of the acetone bodies from fat.

From the following considerations, it will be clear that when glucose is not oxidized in the body, fats are likely to be oxidized *rapidly*, not to carbon dioxide and water but to the stage of the acetone bodies and that the oxidation of glucose leads to the complete oxidation of fats.

We[3] have observed repeatedly that in presence of sodium arsenite, which itself becomes oxidized when added to sodium sulphite solution, the velocity of the oxidation of sodium sulphite by air is markedly retarded. Similarly we have observed that in presence of solutions of carbohydrates, which are themselves oxidized by air when mixed with sodium sulphite, ferrous hydroxide, or cerous hydroxide, the velocity of the oxidation of sodium sulphite or ferrous hydroxide or cerous hydroxide is largely decreased. Moreover, we have arrived at the generalisation that in oxidation reactions, the phenomenon of negative catalyst will be observed when the catalyst is a reducing agent.

Now in normal health, the heat and energy of the body are supplied to the system from the combustion of carbohydrates, fats and proteins. The oxidation of fats is retarded by carbohydrates or less powerfully by proteins, just as the oxidation of sodium sulphite is retarded by sodium arsenite. It seems fairly certain that the presence of either one or two of the above substances

[1] J. Phys. Chem., 30, 144 (1926).

[2] J. Phys. Chem., 29, 376, 799 (1925); Chemie der Zelle und Gewebe, 12, 217 (1925); 13, (1926).

[3] loc. cit. also Proc. Akad. Wet. Amsterdam, 29, 1023 (1921); Z. anorg. Chem., 144, 289 (1925). Cf. Moureu and Dufraisse: Compt. rend., 179, 237 (1924).

(e.g. carbohydrates, fats and proteins), which are undergoing oxidation, retards the oxidation of the third. In presence of an excess of fat, little protein is burnt. It is evident, therefore, that fat in the diet may avoid the consumption of the tissue fat and prevent too large catabolism of tissue protein. The protein sparing qualities of carbohydrates and fats were discovered by some of the earliest students of metabolism and it is well known that carbohydrates is the more efficient of the two in sparing protein, because carbohydrates are more readily oxidized in the body than fats and are more powerful negative catalysts than fats in the oxidation of proteins by air.

When the oxidation of fats is very rapid in the absence of the powerful negative catalyst, glucose, which passes out practically unoxidized as in severe diabetes, it seems likely that complete combustion of fat to carbon dioxide and water does not take place, but intermediate products like acetoacetic acid, β-oxybutyric, etc. are generated. Apparently, the easily oxidizable carbohydrates, which act as negative catalysts in the oxidation of fats, are necessary for the complete oxidation of fatty food materials, the oxidation of both the substances can go on *slowly* and simultaneously. Not only are the carbohydrates themselves effective in preventing the formation of acetone bodies but alcohol, which is likely to be a negative catalyst in the oxidation of fats, has been found to be useful in the prevention of the generation of acetone bodies. Protein will also act as a weak negative catalyst in the oxidation of fats and will prevent, though to a much smaller extent than carbohydrates, the generation of acetone bodies. The importance of these principles to the diet of the diabetic is at once apparent, as it becomes imperative to allow sufficient carbohydrates in the food to carry on the combustion of fats beyond the acid forming stages. It has to be remembered, also that protein is of much less value for this purpose than the carbohydrates themselves. The dangers of the old high protein diet are not yet generally recognized. Protein yields not only a large percentage of glucose (58%) but it also yields a high percentage of acids capable of causing acidosis.

Though there is difference of opinion regarding the fate of glucose in blood when insulin is injected, we have emphasised that it is oxidized in the blood into carbon dioxide and water supplying heat to the body. This view is supported from the following considerations:

Insulin usually gives the following results in the treatment of diabetes:—

(a) Blood sugar is markedly reduced even to normal value.

(b) Glycosuria is abolished.

(c) Acetone bodies are made to disappear from the urine.

(d) The respiratory quotient gives evidence of increased utilisation of carbohydrates.

(e) Definite improvement is observed in the general condition of the patient and in addition the patient reports a subjective sense of well-being and increased vigour for a period following the administration of insulin.

The explanation of the disappearance of acetone bodies is this:—when insulin is injected, the glucose in the system is readily oxidized and this oxidation of glucose to carbon dioxide and water decreases the velocity of the

oxidation of fats in the body. Moreover, complete oxidation of fats to carbon dioxide and water is possible only when the oxidation of fats is slowed down by some suitable negative catalyst, preferably the carbohydrates, which in their turn will be slowly oxidized due to the presence of fats. The mere presence of glucose is not enough for the disappearance of the acetone bodies, but glucose must be oxidized along with the fats in order to avoid the formation of acetone bodies by the rapid oxidation of fats.

Consequently, it seems pretty certain that the disappearance of the acetone bodies from diabetic urine due to the injection of insulin is an effect concomitant with the increased oxidation of glucose.

When insulin is injected, the patient feels a sense of well being and increased vigour and this can only arise when there is increased oxidation of glucose and indirectly more complete oxidation of fats in the body and the system receives an extra amount of energy.

Moreover, we[1] have proved experimentally that in presence of alkalies, the induced oxidation of carbohydrates is greatly facilitated and in presence of acids, the velocity of oxidation is greatly decreased. Consequently the generation of acids like acetoacetic, β-oxybutyric, etc., by the rapid oxidation of fats, greatly decreases the velocity of oxidation of food materials, in the body and is therefore highly detrimental to the body from the oxidation point of view.

It is now well known that insulin is a powerful drug and in overdose, it gives rise to violent symptoms, convulsions, etc., which may be controlled by the intake of glucose or of orange juice. It is well known that in normal health, the blood and other parts of the body contain small amounts of sugar. Now if an overdose of insulin is given, the normal amount of glucose in the body is also burnt and hence convulsions follow.

It is clear, therefore, that insulin does not directly accelerate the complete oxidation of fats to carbon dioxide and water, but it helps the complete oxidation of fats through the oxidation of glucose, which, before the injection of glucose, was passing out practically unoxidized from the diabetic system.

Summary and Conclusion

1. The oxidation of fats is retarded by carbohydrates or less powerfully by proteins just as the oxidation of sodium sulphite is retarded by sodium arsenite.

2. The oxidation of protein is markedly retarded by carbohydrates and fats.

3. When fats are rapidly oxidized due to the absence of the negative catalyst glucose, acetone bodies are likely to be generated in the body.

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[1] Palit and Dhar: J. Phys. Chem., 29, 799 (1925).

4. Apparently the easily oxidizable carbohydrates, which act as negative catalysts in the oxidation of fats, are necessary for the complete oxidation of fatty food materials, the oxidation of both fats and carbohydrates can go on slowly and simultaneously.

5. It seems pretty certain that the disappearance of the acetone bodies from diabetic urine due to the injection of insulin is an effect caused by the increased oxidation of glucose in the body.

Chemical Laboratory,
Allahabad University.
Allahabad, India.
July, 1926.

CHIMIE INDUSTRIELLE SOCIÉTÉ 23, Rue St-Dominique ANNULÉ

818-512

THE DROP NUMBER AND EMULSIFIABILITY

BY R. CHRISTIE SMITH AND MISS I. C. DOW

From the earliest development of emulsions interfacial tension has been connected with emulsifiability. Brücke[1] and Gad[2] both showed that better emulsification was obtained using rancid oils, or oils containing fatty acids, than pure oils along with borax or sodium carbonate solutions, and Quincke,[3] experimenting with various oils and caustic soda solutions showed that the interfacial tensions were lower than with oils and pure water. In 1891 Rachford[4] showed that a pure neutral oil could not be emulsified in dilute sodium carbonate solution. Donnan[5] investigated the drop number of certain oils against alkaline solutions. It was shown that the lowering of the interfacial tension was due to the presence of a soap. The investigation was extended to hydrocarbon oils mixed with members of the fatty acid series in caustic soda solution. The members of the series up to and including the heptylate showed no emulsification, and only a slight lowering of surface tension.

Since then it has been assumed by several investigators that emulsifiability and drop number go hand in hand. For instance Meunier and Maury[6] give the following figures for the emulsifiability of certain oils as measured by the drop number method:—

Neats foot oil	18	Castor oil	9
Olive oil	20	Mineral oil (d 0.934)	9
Linseed oil	18		

and Clayton[7] states that "the first three oils are thus about twice as easily emulsified in water than is castor oil or mineral oil." The following oils have given approximately the same drop number[8] and the deduction is made that their emulsifiability is therefore about the same.

Temp.	25.5°	Arachis	66	Temp.	30°	Palm Kernel	73
	27.5	Cottonseed	65		35	Oleo	66
	30.0	Cocoanut	69				

White and Marden[9] have shown that working with linseed oil or kerosene and sodium oleate and palmitate the emulsifiability increases with decrease

[1] Sitzungsber. Akad. Wiss. Wien, **61 II**, 362 (1878).
[2] E. duBois. Reymond's Archiv Anat. Physiol., **1878**, 181.
[3] Wied. Ann., **35**, 589 (1888).
[4] J. Physiol., **12**, 72 (1891).
[5] Z. physik. Chem., **31**, 42 (1899).
[6] Collegium, **1910**, 277.
[7] "Theory of Emulsions and Emulsification," 11 (1923).
[8] Clayton: Trans. Faraday Soc., **16**, Appendix p. 24 (1921).
[9] J. Phys. Chem., **24**, 616 (1920).

of surface tension, and Jajnik and Ilahi[1] working with the same soaps and a variety of oils (cottonseed, mustard, poppy, etc.) state that the soap solution with the lowest surface tension possessed the greatest emulsifying power.

In spite of that, however, emulsifiability cannot be judged by surface tension alone. As early as 1915 Briggs and Schmidt[2] commented adversely on the drop number as a measure of the emulsifiability, in the case of benzene and water with gum arabic and gelatine. Their results showed

Benzene into Water	87
1% sodium oleate	230
1% gum arabic	61
1% gelatine	23-32

It will be seen that both gelatine and gum arabic give drop numbers in defect of water and yet are both emulsifying agents. Holmes' work on gelatine seems to indicate that it is a case where viscosity rather than surface tension determines the stability.[3] That the drop number is unreliable in the case of soap solutions for determining the emulsifying power has also been noted by Simm.[4]

The relation between the drop number and emulsifiability has now been investigated in the case of various oils e.g. olive, linseed, etc., and water. As has been previously shown cod liver, whale, seal, olive, arachis, coconut have approximately the same drop number while mineral oil is less, and castor oil about half the value.

On emulsifying, most of the oils gave a creamy disperse emulsion throughout, but which on standing tended to break down. By emulsifiability is understood ability to be emulsified, but this implies two factors namely the ease with which the disperse phase is dispersed and the stability of the resulting emulsion. The first factor will certainly be influenced by surface tension and the ease of dispersion will be proportional to the lowering of surface tension, but the second will depend on several other factors besides surface tension and will be indicated by the length of life of the emulsion. So that the measurement of the emulsifiability must take into consideration these two factors and it is here that the drop number method fails. It takes account of the first, but not the second, factor. This is shown by the results given in Table I.

As already stated the emulsions formed immediately had a creamy light coloured appearance, but as time went on the colourd darkened and in some cases three layers were actually visible in the tube. The bottom clear water, the intermediate clearly defined a coarse emulsion of water in oil and the top a fine dispersion of water in oil. In some cases a very fine dispersion of oil in water was obtained along with the principal emulsion of water in oil. The castor oil gave an extremely dilute but stable emulsion of water in oil.

[1] Kolloid-Z., **37**, 139 (1925).
[2] J. Phys. Chem., **19**, 496 (1915).
[3] L. W. Parsons: J. Ind. Eng. Chem., **14**, 797 (1922).
[4] J. Soc. Dyers and Colourists, **42**, 212 (1926).

TABLE I

Temp.	Oil	Drop No.	Emulsifiability	Disperse Phase
20°	Cod Liver	34	0.99	W
	Whale	28	0.98	W
	Linseed	56	0.95	O
	Mineral	21.5	0.87	W
	Seal	32	0.74	W
	Olive	27	0.46	W
	Arachis	30	0.16	W
30°	Cocoanut	30	0.04	O
20°	Castor	15	0.02*	W

No. Estimated.

Experimental

The oils were not specially purified as all the tests were applied to the same sample of the oils.

The Donnan pipette was thoroughly cleaned and filled with the oil and placed in a glass cylindrical jar in a glass sided thermostat. The relative heights of the surface of the water in the jar and the tip of the pipette were maintained constant throughout the experiments. The temperature was maintained at 20°C except for cocoanut oil which was determined at 30°C. The densities of the oils used are given by Lewkowitsch[1] as lying between 0.91 and 0.96. The drop numbers were reproducible in most cases to a drop.

The method of emulsification has been described in detail[2] but may be repeated briefly here. A cylindrical tube with a hole in it, fitted to a shaft, has soldered to its lower end a disc of brass to which on the under side are attached vanes covered with copper gauze. On rotating, liquid is drawn through the hole in the shaft and thrown out through the gauze. The whole fits into a boiling tube and emulsifies conveniently a volume of 40 ccs. i.e. 20 ccs oil and 20 ccs distilled water were placed in the tube and emulsified by the machine revolving 2000 times a minute for two minutes. The resulting emulsion was then transferred to a test-tube and allowed to stand for an hour. During this period the emulsion settles out into three layers: oil, emulsion, water. The fraction of the oil emulsified is read and multiplied by the fraction of the total volume occupied by the emulsion. This product gives a measure both of the percentage of oil emulsified and of the dispersity of the emulsion. The results are given under "emulsifiability" in Table I. The phases were tested by the drop dilution method.

[1] "Chemical Technology and Analysis of Oils and Fats" (1922).
[2] Rev. gén. Colloides, 5, 412 (1927).

Summary

1. An attempt is made to clear up the misunderstanding that has arisen with the term "emulsifiability," and it is pointed out that emulsifiability implies two factors (a) ease of emulsification (b) stability of resulting emulsion.

2. Evidence is produced to show that the drop number measures only the first factor and is therefore not a true indication of emulsifiability.

One of us (R. C. S.) desires to express thanks to the Carnegie Trust for a Grant which enabled this work to be carried out.

Physical Chemistry Department,
University of Glasgow.
May 26, 1927.

THE ELECTRODE POTENTIALS OF BERYLLIUM, MAGNESIUM, CALCIUM, STRONTIUM AND BARIUM FROM THERMAL DATA

BY WENDELL M. LATIMER

A direct method for the calculation of the potential of the Group II metals has been made available through the values of Latimer and Buffington[1] for the entropies of aqueous ions. These values, together with the entropies of the metals and hydrogen gas, permit the calculation of the entropy change, $\triangle S$, for the reaction

$$M + 2H^+ = M^{++} + H_2.$$

The heats of solution, $\triangle H$, of metals in acid are known with greater accuracy than can be ascribed to the majority of chemical reactions. From the values of $\triangle S$ and $\triangle H$ the free energy, $\triangle F$, and the electrode potential, $E°$, may at once be calculated;

$$E°nF = \triangle F = \triangle H - T\triangle S,$$

where nF is the number of faradays of electricity.

Entropies of the Metals and Hydrogen. The values for the entropy of magnesium and calcium, Table I, have been taken from the paper by Lewis, Gibson and Latimer.[2] The entropy of beryllium given by Lewis and Gibson[3] in their original paper is in error owing to a mistake in recording the figure for the specific heat given by Dewar. A recalculation of the specific heat data gives for the entropy at 298° the value 2.4 calories per degree.

In order to obtain the entropies of strontium and barium, use has been made of the equation,

$$S = (3/2)R \ln (\text{at. wt.}) + R \ln (\text{at. vol.}) - (3/2)\, R \ln (\text{m.p.}) + C.$$

This equation[4] holds very well for the group, as is shown by the evaluation of the constant, using the entropies of beryllium, magnesium and calcium. The values so obtained for C at 298°K are 14.5, 14.0 and 14.0, respectively. Since the data for beryllium are not of great accuracy, the value C = 14.0 has been employed in calculating the entropies of the other two elements.

The entropy of hydrogen has been taken as 29.4 in agreement with the figure given by Lewis, Gibson and Latimer.[5]

Entropies of Metal Ions. The values for the entropies (referred to $H^+ = 0$) of magnesium, calcium and barium ions in hypothetical one molal solution at 298°K, Table I, are those given by Latimer and Buffington,[6] and the values

[1] Latimer and Buffington: J. Am. Chem. Soc., **48**, 2297 (1926).

[2] Lewis, Gibson and Latimer: J. Am. Chem. Soc., **44**, 1008 (1922).

[3] Lewis and Gibson: J. Am. Chem. Soc., **39**, 2554 (1917).

[4] Although this equation is empirical it may be derived from the Planck equation for the entropy of a system of oscillators, $S = 3R \ln kT/h\nu$, and the Lindeman relation for the vibration frequency of metals, $\nu \propto T_{m.p.}^{1/2} M^{-1/2} V^{-1/6}$. See also Buffington and Latimer: J. Am. Chem. Soc., **48**, 2317 (1926); Eastman: **45**, 80 (1923).

[5] Lewis, Gibson and Latimer: J. Am. Chem. Soc., **44**, 1008 (1922).

[6] Latimer and Buffington: J. Am. Chem. Soc., **48**, 2297 (1926).

for beryllium and strontium have been calculated from the relation for the divalent ions given in the same paper;

$$S_{aq.\ ion,\ 298°K} - S_{gas\ ion} = -9.5 + 94.5(1/r),$$

where $S_{gas\ ion}$ is the value given by the Sackur[1] equation for monatomic gases at 298°K and 1 atmosphere, namely,

$$S_{gas\ 298°K} = 3/2\ R \ln \text{at. wt.} + 25.7,$$

and r is the ionic radius in Ångström units. The equation is based upon the original values of Bragg and Bragg[2] for the radii in which sodium is 1.75×10^{-8} cm. If the newer values are used the constants of the equation are changed, but the validity of the relation remains, since the change in the values for the radii simply involves the rather arbitrary choice of a reference ion. The calculations have been made taking the radius of beryllium ion as 1.11 and that of strontium as 1.95 Å.

Heats of Reactions. The heat of solution of a number of metals in acid has been made the subject of a careful investigation by Richards and co-workers. Unfortunately they have studied only one of the Group II metals, magnesium.[3] Their value is given in Table I. The values for calcium, strontium and barium are from the determinations by Guntz and Benoit.[4] The heat of solution of beryllium in acid has been calculated from the following experimentally determined heats:

$$Be + \tfrac{1}{2}O_2 = BeO \quad ; \quad \Delta H, -134.2 \text{ kg. cal.}$$
$$BeO + 2H^+ = Be^{++} + H_2O; \quad \Delta H, -17.0 \text{ kg. ca.}$$
$$H_2O = H_2 + \tfrac{1}{2}O_2 \quad ; \quad \Delta H, +68.3 \text{ kg. cal.}$$

The first reaction heat is that given by Moose and Parr,[5] the second is from a survey of several values by Matignon and Marchal,[6] and the third from the calculations of Lewis and Randall.[7]

TABLE I

Summary of Data

	Entropy of metal cal/deg	Entropy of metal ion cal/deg	298° × △S kg. cal.	△H kg. cal.	△F kg. cal.	E° volts
Be	2.4	−43.5	−5.6	−82.9	−77.9	−1.69
Mg	8.3	−19	+0.6	−110.2	−110.8	−2.40
Ca	10.6	−9	+2.9	−129.8	−132.7	−2.87
Sr	13.3	0	+4.2	−130.2	−134.7	−2.92
Ba	15.1	+4	+5.4	−128.6	−134.0	−2.90

[1] Sackur: Ann. Physik, **40**, 67 (1913). See also Lewis, Gibson and Latimer: loc. cit.
[2] Bragg and Bragg: "X Rays and Crystal Structure," (1924).
[3] Richards and Burgess: J. Am. Chem. Soc., **32**, 431, 1176 (1910).
[4] Guntz and Benoit: Compt. rend., **176**, 219 (1923).
[5] Moose and Parr: J. Am. Chem. Soc., **46**, 2654 (1924).
[6] Matignon and Marchal: Compt. rend., **181**, 859 (1925).
[7] Lewis and Randall: "Thermodynamics and the Free Energy of Chemical Substances," (1923).

The reliability of the electrode potentials for the hypothetical one molal solutions of the ions is dependent largely upon the accuracy of the heats of the reactions, as an error of one entropy unit affects the potential by only 0.006 volt, and with the exception of beryllium the $\triangle S$ values are probably not in error by more than 2 entropy units. It is difficult to estimate the accuracy of the heats of solution, but calorimetric determinations of this nature should easily be made with an accuracy of one percent, while the value of Richards for magnesium is probably accurate to 0.2%. Because of the difficulties of obtaining the conditions of complete reversibility, the few direct measurements which have been made with these electrodes have been subject to wide variations. Probably the most accurate work is that of Tamele[1] who gives for the potential of the calcium electrode 2.76 volts.

Acknowledgement is made to Mr. Charles Kasper for assistance in checking these calculations.

Summary

The values for the entropies of the aqueous ions, together with the entropies of the elements and the heats of solution of the metals in acid, have been used to calculate the electrode potentials of beryllium, magnesium, calcium, strontium and barium.

Department of Chemistry
University of California
Berkeley, California.

[1] Tamele: J. Phys. Chem., **28**, 502 (1924).

NEW BOOKS

Surface Equilibria of Biological and Organic Colloids. *By P. Lecomte du Noüy. 23 × 16 cm; pp. 212. New York: Chemical Catalog Company, 1926. Price: $4.50.* The chapters are entitled: technique; drop of the surface tension of colloidal solutions as a function of time; monomolecular layer of serum constituents; sodium oleate; ẽgg albumin; characteristics of immune serum; influence of colloids on the crystallization of sodium chloride; surface equilibrium of complex colloidal solutions; interfacial tension; colloidality of solutions of proteins, serum, and plasma; general conclusions.

"A survey of the advancement of knowledge brings the realization that the progress of science has been achieved through the constant improvement of experimental technique. This, of course, does not apply to the immense strides made by the speculative genius of men like Newton, Maxwell, and Einstein, who belong in a class apart," p. 19

"There are about twenty different methods for the measurement of the surface tension of liquids. These methods have been reviewed in detail by A. Ferguson, who clearly demonstrates, in a remarkably thorough paper, that only three need be considered; the so-called Jaeger method, the method based on the photography of large air-bubbles produced in the liquid, and the ring method.

"Speaking generally, the methods can be divided into two principal categories: those which depend on a knowledge of the angle of contact and those which do not. Those which depend on it are unsatisfactory when applied to colloids. The others may be divided again into two principal classes if one considers them from the special standpoint of colloidal solutions: 1st, the dynamic methods; 2nd. the static methods," p. 21.

The author has improved and adapted the ring method, "which was impractical as devised by Sondhaus, Timberg, and Weinberg," so that the following conditions are fulfilled: "employment of a small quantity of liquid; great rapidity of measurement (about 20 seconds); possibility of a large number of measurements in a short time; elimination of systematic causes of error; precision of the order of 1/10 of a dyne (that is 0.14 percent for water and 0.3 percent for alcohol and ether); easy standardization in absolute units (dynes /cm)," p. 23.

Glasses can be cleaned by boiling for two hours with acidified bichromate, rinsing with distilled water, and drying in a place where they are protected from dust. "Under such conditions the glass is clean. Nevertheless its 'wetability' is not always perfect. As a rule, it will wet if employed immediately after this treatment, but watch glasses which will wet uniformly on the first day often act like greasy glass after three or four days. This phenomenon is not well understood, but Professor Devaux, who has made a remarkable study of the 'wetability' of surfaces, has suggested a very simple and absolutely efficacious method to correct this fault. Flame the glass for a second or two over a Bunsen burner, taking care that the surface destined to be wetted is in contact with the flame. After cooling, water adheres to the surface in an absolutely perfect manner, a condition particularly essential when watch glasses are used to make measurements, for in certain of our experiments the free surface of the liquid must be known very exactly and this is only possible when it is perfectly circular.

"There is another reason why the wetability must be perfect. A platinum ring with a mean diameter of 12.73 mm. (circumference 4 cm.) is used. For exact measurement it is necessary that the surface of the liquid may be considered as undeformed when the ring lifts a small mass of this liquid above its level. Theoretically, the measurements should be made in a vessel the diameter of which is large in comparison with the ring. This is easy to realise when considerable quantities of liquid are used. But in devising this instrument the aim was to obtain precise measurements with the least possible amount of liquid. The smallest possible limits for the dimensions of the vessel when a ring of 12.7 diameter is used were determined experimentally. It was found that the minimum diameter was of from 5 to 8 cm. when the liquid did not wet the glass, but only of 3.5 cm. when the wetability

was perfect. Now in the watch glasses used by us, two cubic centimeters of water spread over a circle of 4.1 to 4.4 cm. in diameter, which is more than necessary. However, this is only true when the glass is thoroughly wet; that is, if when using pure water the line of demarcation between the glass and the water is invisible," p. 30.

"When in studying the surface tension of any colloidal solution with the preceding technique, measurements of the solution in a watch glass are taken every two minutes, for instance, it is found that the value of the tension decreases regularly. At the end of two hours it appears fairly constant in most cases; but if another measurement be taken after twelve or twenty-four hours, it is generally observed that another decrease has taken place, although of a much smaller magnitude than the first. This is the fundamental fact on which all the following work is based. Some colloidal salts and colloidal oxides, however, such as arsenious sulphide, ferric hydroxide and manganese dioxide, did not show any drop. After a certain length of time depending on the conditions of the experiment, a stable value is attained. This is the static value of the surface tension," p. 35.

"When concentrations around 1/10,000 are used for serum, it is found that the initial tension is about that of pure water. A few minutes later the tension is already lowered and its fall will continue regularly following a logarithmic law. This law cannot easily be expressed by a simple equation, for the curve becomes a straight line at high dilutions, at 1/20,000 for serum, and at 1/100,000 for sodium oleate, for example. The surface tension of water cannot begin to increase until the surface layer is invaded by a sufficient number of molecules. The tension does not change as long as the number of adsorbed molecules is so small that there is a certain distance between them. This delay in the beginning of the phenomenon can be observed at 1/10,000 for serum but is much more marked at 1/20,000. Thirty minutes elapsed in the latter case before a slight decrease in the surface tension of water could be observed. The fall is of 3 dynes in the fifteen minutes that follow and the rate of the fall remains nearly constant until equilibrium is attained," p. 46.

"It has been stated that, according to our hypothesis, the thickness of the adsorbed layer was of the order of 35 Ångstroms or 3.5 $\mu\mu$. If all the amino-acids, lipoids, fats, etc. are included, it would be equal to about 40 Ångströms. It is not without interest to mention the results obtained by Fricke. By using an entirely different method, based on the measurement of the electric resistance of a suspension of red cells in Ringer solution, he arrived at the conclusion that the thickness of the membrane of the red cells was 33 Ångströms. This order of magnitude (3 ten millionths of a millimeter) cannot possibly be considered as applying to a real membrane. The similarity of the figures would therefore indicate that what Fricke measured was really the thickness of the monolayer, which view he has recently adopted. Dr. Fricke assumed, and his measurements have proved, the existence on both sides of the "membrane" of two electric charges, equal in value and opposite in sign. It is impossible to explain otherwise the values obtained. The identical orientation of the molecules, forecast by the writer in 1922, is a necessary consequence of Fricke's experiments. However, these figures must not be considered as rigorously accurate. They merely indicate an order of magnitude. But we may safely say that, considering the precision of the experiments, 4.1 $\mu\mu$ may be taken as an upper limit, and 3.3 $\mu\mu$ as a lower limit of the thickness of the adsorbed monolayer. It will be shown later that when serum is diluted in physiological salt solution the proteins adsorb part of the salt and carry it to the adsorbing surfaces. There is therefore reason to think that the oriented monolayer also contains a certain proportion of salts," p. 85.

"A simple and logical explanation, therefore, of the three minima, is the polarized organization at each minimum, of a single layer of molecules in the surface layer. The first minimum is due to the vertical orientation of the molecules; the second, to their horizontal orientation, and the third to a rotation of these molecules around their horizontal axis. It therefore becomes possible to calculate, as has been done for serum, the thickness of the monolayer corresponding to these three critical concentrations. This leads to three different dimensions for the molecule. The specific gravity of sodium oleate was found to be 0.821. The greatest care was taken in determining this value which coincides exactly with the

value published in the Beilstein and the Landolt tables. Thus the three dimensions of the volume occupied in space by one molecule of sodium oleate ($C_{17}H_{33}COONa$) are found to be:

12.30×10^{-8} cm.
7.56×10^{-8} cm.
6.64×10^{-8} cm.

"The length of the molecule of oleic acid ($C_{17}H_{33}COOH$) found by Langmuir is 11.2×10^{-8} cm. He obtains a value of what he terms the mean diameter by extracting the square root of the mean area occupied by the molecule. This is equal to 6.8×10^{-8} cm.^{2} The method used by Devaux and Langmuir did not enable them to obtain an idea of the shape of the space occupied by the molecule of the fatty acid in a monolayer. Their experiments did not indicate the existence of a monolayer of horizontal molecules of oleic acid. The mean area occupied by a single molecule was obtained by measuring the total surface of the liquid covered by the monolayer which was then divided by the number of molecules present. The square root of this figure expresses the length of the sides of the plane section assuming that this section is a perfect square. The figure of 6.8 Ångströms for this dimension is consequently based on an assumption which nevertheless allowed Langmuir to state that molecules were not spherical," p. 96.

"From the dimension obtained for sodium oleate it is clear that the horizontal section of this molecule is not a perfect square but a rectangle, measuring: 7.56×6.64 Ångströms. The surface of this rectangle is 50.2×10^{-16} cm.^{2} while the surface of the horizontal section of the oleic acid molecule is, according to Langmuir, 46×10^{-16} cm.^{2} The difference of 4.2×10^{-16} cm.^{2} may be due to the presence at the end of the molecule of the large sodium atom which is also responsible for the difference in the length of the two molecules *i. e.*, 1.1×10^{-8} cm. If the atoms were disposed in a straight line the difference would be, greater and both molecules would be longer, but it is known that an angle of approximately 109° exists between the valences of the carbon atom. Consequently, in a carbon chain, the atoms are disposed in zig-zag fashion and the increase in length of 1.1 Ångström represents the projection on the vertical axis of the molecule of the distance between the last oxygen atom and the sodium atom," p. 99.

Wilder D. Bancroft

The Structure of the Atom. *By E. N. da C. Andrade. Third edition, revised and enlarged. 22 × 14 cm; pp. xvii + 750. London: G. Bell and Sons, 1927. Price: 30 shillings.* The rapidity of growth of knowledge concerning the structure of the atom is without parallel in the annals of science. At no previous stage, has the attention of so many able minds been concentrated on the investigation of one group of problems as is the case at the present day. The rapidity with which hypotheses are enunciated, tested, and either rejected or embodied in the science of atomistics is bewildering to anyone who is not directly engaged on research on the subject. It is thus very desirable that a critical and comprehensive survey of the diverse ramifications of atomistic physics should be available, not only to workers in the field, but also to those engaged in research in collateral sciences. There can be little doubt in the minds of both classes of readers that this need has been met by the volume of Professor Andrade.

The remarks made by Francis Bacon concerning the Schoolmen that "they with infinite agitation of wit spun out of a small quantity of matter those laborious webs of learning which are extant in their books" is peculiarly appropriate to modern speculations on the structure of the atom. The views of the schoolmen had not been adequately subjected to the test of experiment and this is also the case for the hypotheses of the twentieth century. The author, who has had a wide knowledge of the history of the development of science has shown his wisdom in the care with which he has made his selection from among the current hypotheses on the structure of the atom. He has selected that modicum of hypothesis necessary to illuminate the whole of his subject but not every corner thereof!

The subject matter of the present edition, which has been completely rewritten, is divided into two parts, the first concerning the nucleus and the second the extra-nuclear structure of the atom. The large number of experimental facts which have been accumu-

lated concerning the passage of corpuscles through matter are discussed in Chapters II and IV, and are applied in a general consideration of the shape, packing and dynamics of the nucleus in Chapter VIII. The interpretation of the experimental results leads to the definite conclusion that the laws of classical mechanics and electrodynamics hold down to very small distances and have established securely the nuclear structure of the atom. Of interest to chemists is the conclusion that the departures from sphericity of the nucleus may modify materially the arrangement of the electronic orbits.

The laws of radioactivity, the origin of the α and β particles and the γ-rays, positive rays, and the atomic number are discussed in the remaining chapters of the first section. The evidence in favour of the view that energy levels occur in the nucleus is presented in a very clear and highly instructive manner.

Preceding the second part of the book, a preliminary account of optical spectra is given which is mainly descriptive in character. This is followed by a more detailed account of the dynamic models of hydrogen-like atoms with circular and elliptical orbits due to Bohr and Sommerfeld. Chapter X is devoted to the hydrogen-like atoms with two quantum numbers and then follows an account of the optical spectra of the general atom, the nature of the electronic orbits, and the general scheme for representing the spectra. The duration of the excited states of atoms, and of those of metastable atoms are discussed. The occurrence of metastable states has a decided chemical bearing, especially as regards helium for in the metastable 1^2S_1 state the helium atom possesses a hydrogen structure and should be capable of chemical combination. Manley has shown that helium combines with mercury but not as the author states to give HgHe.

The experimental methods of determining excitation and resonance potentials and their theoretical significance are given in the following chapter with an extensive account of the Saha equation and its application to astronomical problems.

The X-ray spectra have played a very large part in the elucidation of the physical basis of the periodicity of properties of the elements, and in the development of the theory of spectra. These are dealt with in Chapter XIII. Special reference is made to the relativity and screening X-ray doublets and the relationship between X-ray and official spectra. A complete level scheme for X-ray spectra is given..

The discussion of the periodic properties of the elements is continued from the standpoint of Bohr's survey of the subject, and a very brief summary of coordination compounds and co-valency is included in the following chapter.

The multiplet structure and the anomalous Zeeman effect is discussed at great length, and the recent developments of the theory which have been necessary to explain the anomalies which occur are elaborated in detail. With reference to these theories, the author expresses the following opinion—'the quantum theory has become in its higher branches, a collection of numerical receipts to which a superficial resemblance to a coherent mathematical theory has been given to hide its *ad hoc* character!

The magnetic properties of atoms, the recent work of Gerlach and Stern on atomic rays, the static atomic models, and a comparison between the wave and quantum theories are other branches of the subject which are described in this very comprehensive treatise.

An unusual feature for a book which embodies so much of theoretical interest is the attention paid by the author is the description of experimental method. This method of presentation makes the book of value to a wider circle of readers than would otherwise be the case. Its usefulness is enhanced also by the clarity with which the physical assumptions underlying the mathematical calculations are presented. The arguments can be readily followed by those who have but little mathematical knowledge.

The diagrams are excellent and a very good index is provided.

W. E. Garner

Practical Organic and Biochemistry. *By R. H. A. Plimmer. New edition. 25 × 17 cm; pp. 578. London: Longmans, Green and Co., 1926. Price: 21 shillings.* Professor Plimmer's famous work remains one of the pioneer text-books of biochemistry. Conceived originally as a practical manual of physiological chemistry for medical students, it ex-

panded with the years and the experience of the teacher to embrace an introduction to organic chemistry moulded particularly toward the comprehension of the chemistry of biological material. As such it brought within the covers of one volume both the pure and applied sections of organic chemistry required by the medical curriculum. At the same time its scope far exceeded these modest requirements since it sought to give a "nearly complete statement of the whole subject." Its comprehensiveness and authority won for it a prominent place as a reference book in laboratories engaged in the analysis of biological material.

The present edition witnesses extensive remodelling of the scope and character of the book. Persuaded that the student of biology was inevitably embarrassed by the extensiveness of the treatment of the more complex biological substances the author has deleted most of the chapters which were devoted to such groups as the animal and vegetable pigments, the terpenes and sterols, the tannins and the alkaloids. This unquestionably renders the book more attractive to the elementary student although many biochemists will regret the disappearance of information upon which they were wont to rely. The earlier section dealing with the chemistry of the simpler groups of organic compounds has been extended so that the whole treatise now forms a more satisfactory general course in the subject.

The balance between theoretical and practical instruction is not easy to strike in a limited volume. In its present form Professor Plimmer's book seems to offer as satisfactory a compromise as is possible. At the same time the book suffers from the defect that its theoretical argument has grown around a course of practical exercises. The result almost inevitably, has been that the treatment is not such as to hold the interest of the student apart from his practical experiments.

The method of the author is the classical method of organic chemistry seeking always to define a problem in the rigid language of molecular structure. Where this does not suffice, as in the chapters devoted to the chemical basis of physiological mechanisms, the lessons are not attractive. The student of biology who asks of chemistry a logical strategy for the attack upon the problems of physiological function will find little inspiration in the chapteres devoted to such questions as enzyme action, colloidal behaviour, respiration and metabolism. The author appears to be content to leave to the teacher of physiology the contribution of chemistry to the dynamics of living systems. How, by applying chemical knowledge to the elucidation of vital phenomena, can the teacher hope to mitigate the heavy discipline of chemical method and practice which he seeks to impose upon the physiological student?

R. K. Cannan

Lehrbuch der Enzyme. *Chemie, Physikalische Chemie and Biologie. By Carl Oppenheimer with the collaboration of Richard Kuhn. 25 × 17 cm; pp. ix + 660. Leipzig: Georg Thieme, 1927. Price: 33 marks, bound 36 marks.* Chemists in general and biochemists in particular owe a debt of gratitude to Prof. Oppenheimer for the production of this condensed—it can even yet scarcely be called short—version of his monumental work "Die Fermente und ihre Wirkungen," the fifth edition of which was completed last year.

The idea of the author was to provide a book unhampered by excess of detail from which the reader could nevertheless obtain a sound knowledge of the subject. Anyone especially interested in some particular branch of the subject could refer for further information to the detailed treatise. In this he has been entirely successful and the use of the two books in conjunction is greatly facilitated by the fact that the numbering of the paragraphs adopted in the larger work has been retained in the smaller, as well as the division into chapters and sections (Hauptgruppen & Hauptteile). The chapter on Physical Chemistry and Kinetics, in which the author has had the advantage of the collaboration of Dr. R. Kuhn (Hauptteil IV) occupies 86 pages and does not differ essentially from the corresponding section of the Treatise. It has, however, been necessary, so rapid has been the stream of progress, to make numerous modifications or in many cases to rewrite whole sections. The book thereby acquires a character of its own, and will certainly be found of the greatest value both to students of biochemistry and to the general scientific reader. It is pro-

vided with a good subject index. For bibliography recourse must be had the larger book, the only references cited being the more important ones of the last two years.

Astounding progress has been made during the last five years in our knowledge of the enzymes, although it is not yet possible to say definitely what they are. The greatest success has been attained by the development of methods by which many enzymes have been freed from a large proportion of the attendant inactive matter, and, what is at this stage perhaps even more important, from other enzymes.

In this way for example, the tangle of the digestive enzymes has been to a large extent unravelled. Trypsin from the pancreas is a mixture of al least three things: 1. An inactive tryptase (usually, but it now seems erroneously, termed trypsinogen) which has no action on the more complex proteins but hydrolyses peptones and some protamine as far as the polypeptide stage. 2. A peptidase, which has the power of hydrolysing ploypeptides. 3. A prokinase, which gradually becomes converted into active kinase and thus gives rise to the spontaneous activation of the "trypsinogen." When it is removed, as it can be by adsorption methods, no spontaneous activation occurs. The kinase produced from this prokinase is identical with that contained in the intestine (enterokinase) and is a co-tryptase, which renders possible the proteolytic action of the tryptase on the more complex proteins, but does not alter its properties in any way. This is proved by the fact that the kinase can be removed from the active mixture by an appropriate adsorbent leaving behind the inactive tryptase, capable of being reactivated by the addition of a further quantity of kinase.

A similar complication has long been known to exist in such a process as the coagulation of the blood and is reveled in many other cases, notably in that of the utilization of carbohydrate, which has been investigated by entirely different methods.

This singular complexity of the methods employed by the living organism for carrying out at a low and almost constant temperature and in a nearly neutral medium, the chemical reaction necessary for its welfare, constitutes one of the most striking and fascinating results of biochemical research. No one of scientific mind reading the account of these discoveries can fail to have his imagination stimulated and his deepest interest aroused.

Arthur Harden

Treatise on Thermodynamics. *By Max Planck. Translated by A. Ogg. Third edition. 22 × 14 cm; pp. xiv + 297. London: Longmans Green and Co., Price: 21 shillings.* Professor Planck's treatise, which appeared first in German in 1897, has established itself as a classic and seven German editions have appeared, the last, from which the present translation was made, in 1922. Since that date some changes have taken place and in one or two places the translation no longer representes the present state of the subject. For example, the theory of Ghosh on strong electrolytes still finds a place in the text . It is to be regretted that the translator has not seen his way to discuss this part of the book with the author, so that a more accurate and modern treatment could have been adopted.

Planck's book, however, is not addressed to readers who wish to find a detailed treatment of the *minutiae* of the latest hypotheses. The subject is one which, as the author emphasizes, is in no way dependent upon hypotheses of any description for its fundamental propositions and general deductions. In the applications to specific problems, naturally, some assumption has nearly always to be made. The properties of ideal gases and dilute solutions are hypothetical, and those of actual gases and solutions are either hypothetical or empirical. Such matters are introduced by the author more as illustrative examples of general equations or methods than as having any validity apart from this; they are looked down upon from a purer ether and from an altitude such that they appear in their proper proportions. It would have been well, all the same, to have excluded hypotheses which have been borne off the field of practical strife and to have replaced them by others which still have their day.

The treatment begins with a careful survey of the First Law, which the author says is no longer disputed. This is stated in a general form depending on the definition of the *energy* of a system as a magnitude which is a function of the momentary condition of the system and equal, with reference to an arbitrarily selected normal state, to the algenraic sum of the mechanical equivalents of all the effects produced outside the system when it

passes in any way from the given to the normal state, this sum being independent of the manner of transformation. All the general propositions which follow from this are next deduced.

The Second Law is dealt with in a most careful and instructive manner. It is considered as defining the direction in which a process takes place in nature, and the fact of experience that natural processes tend to take place in a particular direction, which is closely connected with the irreversibility of processes in the thermodynamic sense, leads to the assumption that there exists in nature for each system of bodies a quantity, called the *entropy*, which in all changes of a system either remains constant (in reversible changes) or else increases (in irreversible changes). This is taken as the statement of the Second Law. The deduction of the general conditions of equilibrium, with the introduction of the thermodynamic functions, follows, and the rest of the book then deals with the applications of these general equations to various important systems. In the section devoted to heterogeneous systems a careful and detailed deduction of the phase rule is given, and a simple case of a thermodynamic surface is treated. Nernst's theorem, considered as a means of defining the absolute value of the entropy of a system in special cases, closes the book.

Every student who wishes to comprehend the real fundamentals of Thermodynamics, as distinct from the acquisition of a certain facility of using equations and formulae which are of restricted validity, may be recommended to study Planck's book whatever others he may use. It is the work of a master who has comprehended the subject in its entirety, given to it a marked individuality, and set it down with an unusual clearness and logical sequence which the excellent translation of Dr. Ogg has preserved in an admirable manner.

J. R. Partington

Die Zerstäubungserscheinungen bei Metallen. *By Joseph Fischer. Vol. 19, No. 1. 25 × 17 cm; Berlin: Gebr. Borntträger, 1927. Price: 4.80 marks.* Until quite recently the phenomenon of "sputtering" offered a curiously neglected field of research, in which practice had far outstripped theory. Grove in 1853 seems first to have recorded that electrical discharge tubes gradually blackened, and to have connected the blackening with the deposition of material from the cathode. When X-ray tubes first became the fashion, sputtering was of great importance; for it was soon found to be closely connected with the "hardening" of the tube, the bugbear of early workers. Later sputtering ceased to be merely a nuisance and became a valuable tool, widely used for the preparation of thin films of metal. Today mirrors, high resistances, bolometer strips, conducting fibres for galvanometers and electrometers are all prepared by sputtering, which has the advantage over alternative methods that almost any metal can be deposited uniformly and coherently on almost any support, and that the rate of deposition is easily controlled.

But long after sputtering had been brought under practical control, an adequate explanation of it was still lacking. Many distinguished physicists had attacked the problem, making the obvious experiments and propounding the obvious theories. But the experiments were laborious and all the theories much too simple. The rate of sputtering depended on the nature of the metal and of the gas through which the discharge passed, but it was not simply connected with any single property of them. The effect of the electrical conditions was even more difficult to interpret, because no adequate theory of the discharge was available, explaining exactly the rules of positive ions and electrons in the neighbourhood of the cathode.

In 1912 Kohlschütter, who had been an active worker, summarised the position and could hardly conceal, even from himself, how fragmentary our knowledge was. And there the matter rested till 1923, when interest revived. The two General Electric Companies (English and American) produced a new technique; but it was Günther-Schulze of the Reichsanstalt, using the old one, who finally found the clue. He distinguished between two kinds of sputtering, one due to the formation and decomposition of a gaseous compound of the metal; the other (in practice the more important one) due to the evaporation of the metal by intense local (perhaps molecular) heating where the positive ions impinge on the cathode,

and the diffusion of the vapour through the gas to the walls. Previous theories were inadequate because they neglected the distinction between the two types and the diffusion in the second type.

Herr Fischer has had the misfortune to write his monograph just too early; the final step was taken while it was in the press. Since he confines himself to the theoretical aspect of the matter, it would be idle to pretend that his work has not suffered by his misfortune; for discarded theories are mere rubbish to all but antiquarians. It is all the more unfortunate because his treatment is admirably clear and suggestive. Perhaps he is a little too apt to estimate the importance of researches by their length; and perhaps he would have been wiser to omit all reference to subjects which he did not propose to treat thoroughly, such as actions similar in their result to sputtering but different in their origin. But otherwise his account of the work that had been published when he wrote could hardly be improved. *N. R. Campbell.*

Three Lectures on Atomic Physics. *By Arnold Sommerfeld. Translated by H. L. Brose. 19 × 13 cm; pp. 70. New York: E. P. Dutton and Company, 1926. Price: $1.00.* These lectures were apparently given at University College, London, at some unspecified time. The titles of the three lectures are: general remarks on atomic physics, in particular on the spectra of hydrogen and helium; the general system of the complex terms; chemical bonds and crystal structures. The publishers say: "These lectures deal with recent developments of the quantum theory. The quantum numbers, n, k, j, m, etc., are introduced in the first lecture, and a new theory of the hydrogen atom is developed, according to which this atom has a structure analogous to that of the alkali metals. The second lecture is concerned with the general construction of terms of any multiplicity, with the definition of primed and unprimed terms and their selection rules, with Pauli's principle of uniqueness, etc. The third lecture deals with the periodic system of the elements and the tetrahedral structure of certain elements of the fourth group. In this connection the problem of chemical linkages is discussed in general, but with special reference to the nature of nonpolar compounds."

"What are at present the most acute questions of atomic physics? First and foremost we may certainly place the problem of the nature of light. The question as to whether light is undulatory or corpuscular, which seemed to have been decided a century ago, now presents itself again in a more insistent and definite form. How hopeless this question is at the moment is illustrated by the unsuccessful attempt made by Bohr, Kramers and Slater to link up the two divisions of optical phenomena through a compromise which sacrificed the principle of energy. Unfortunately I have nothing new to report upon this question and am forced to do what all other physicists nowadays do; that is, to treat light and Röntgen rays sometimes as quanta and sometimes as waves," p. 2.

"It is more than probable that we shall sooner or later arrive at a fifth quantum number. This will be the "fine-quantum-number" f, according to a proposal by Ruark. Its province will be the explanation of satellites of spectral lines (observed particularly in the case of the heavy elements Hg, Tl, Bi). Just as n or n_r differentiates the members of a series, k the various series, j the various levels of the multiplet terms, m the magnetic levels of these terms, so f will have to characterize the finer sub-division of the terms. Before such a fifth quantum number may be introduced, it must be decided whether the combination principle also holds for satellites, that is, whether the satellite-lines are given by the energy difference between an initial and a final state. It will be a beautiful and at the same time difficult task for the spectroscopists to solve this problem experimentally. Theoretical spectroscopists will have to wait until the experimenters have preceded. Theory, which follows in the wake of practice, is nevertheless not without its uses, as practical spectroscopists of the present day know," p. 12.

"Our method of designating and standardising the quantum numbers proves itself the simplest and most direct expression of the facts of observation. I should like to conclude by recommending this nomenclature and method of standardisation to the great school of English spectroscopists," p. 55.

"We arrive at the conclusion: the theory of the periodic system shows in what elements completed sub-groups are to be expected. Not only the shell of the inert gases, consisting of 8 electrons, but also the shell of 18 electrons, and in particular that of 2 electrons are realised in stable compounds. On the other hand, the 4-shell manifests itself in the tetrahedral crystal structure and points to the same type of binding as in diamond. The binding is effected not only by polar ions of the usual sign but probably by neutral or nearly neutral atoms.

"We may expect that the great chemical problem of the nature of the non-polar bond will be helped forward materially by an exact investigation of tetrahedral crystal structures," p. 69.

Wilder D. Bancroft

A Survey of American Chemistry. *Vol. I. Edited by William J. Hale. 21 × 14 cm; pp. 257. New York: Chemical Catalog Company, 1927. Price: $2.00.* In the foreword the editor says that the Division of Chemistry and Chemical Technology of the National Research Council has essayed [?] to bring together in this volume a number of articles from well-known scientific authorities "in order that the chemists of America may be given a perspective of the advance made in their several fields of research and in order that the importance of certain prospective researches may be adequately emphasized by those most qualified to express opinion."

The volume contains thirty-four surveys: aluminum, by F. C. Frary; chromium, by C. G. Fink; copper, by W. H. Bassett; iron and steel, by H. M. Boylston; lead, by G. W. Thompson; magnesium, by J. A. Gann; nickel, by P. D. Merica; radium and radioactivity, by S. C. Lind; rare earths, by H. E. Miner; zinc and cadmium, by W. R. Ingalls; heavy acids, by W. A. Pratt; salts and non-metallic inorganic substances, by J. R. Withrow; metallo-organic compounds (elements of the fourth group), by C. A. Kraus; metallo-organic compounds (other elements), by F. C. Whitmore; aliphatic compounds, by E. E. Reid; carbocyclic organic compounds, by Roger Adams; heterocyclic organic compounds, by T. B. Johnson; azo dyes and intermediates, by E. F. Hitch; vat dyes and intermediates by E. K. Bolton; pharmaceutical chemistry, by F. O. Taylor; organic medicinals, by M. T. Bogert; proteins, by P. A. Levene; nucleic acids, by P. A. Levene; rubber, by W. C. Geer; cellulose, by H. LeB. Gray; sugar chemistry, by C. S. Hudson; fermentation industries, by C. L. Gabriel; biochemistry, by D. D. Van Slyke; photochemistry, by H. S. Taylor; colloid chemistry, by H. B. Weiser; catalysis, by H. S. Taylor; explosives, by C. E. Munroe; water and sewage, by Edward Bartow; coöperative research between industries and universities, by W. J. Hale.

The editor has picked his authors well and the volume is an interesting one; but the desirability of this kind of book is not evident. If any other people, the Germans for instance, had written a survey of chemistry, leaving out all reference to American work, we would have objected very strongly and we would have said that science recognizes no geographical boundaries, etc, etc. It is apparently all right if we do a worse thing than the Germans ever dreamed of doing. The whole thing is frankly a small-town advertizing project. The reviewer believes that this volume should never have been published; that the second annual survey, now nearly written, should not be published; and that the series should be discontinued as soon as possible. It is perhaps fair to add that the reviewer seems to constitute a well-organized minority of one on all three points.

Wilder D. Bancroft

Physikalische Chemie, *Part II. By Alfred Benrath. 22 × 15 cm; pp. x + 192. Dresden and Leipzig: Theodor Steinkopff, 1925. Price: 8.50 marks paper, 9.70 marks bound.* The first section of this book was reviewed three years ago (**28**, 527). This part deals with thermal and photochemical equilibria and reaction velocities. The first chapter deals with equilibria in heterogeneous systems; the second chapter covers reaction velocities in the gas phase, in the liquid phase, and in heterogeneous systems; while the third chapter takes up photochemical changes.

The author inclines to Michael's view—without mentioning him—that most reactions are preceded by the formation of an addition compound, p. 17. It was new to the reviewer that under very high pressures, an iodine hydrate is formed, which is purplish violet in color, p. 30. Ethane and ethylene each form a hydrate containing two of water, p. 31. The reviewer does not admit that compounds between fatty acids must be formed because the solubility of one fatty acid in carbon tetrachloride is increased by the addition of another acid, p. 32, any more than he admits that benzene and alcohol must form definite chemical compounds because alcohol increases the solubility of benzene in water. The statement is made on p. 35 that mannit is not precipitated from aqueous solution by addition of alcohol. Since cane sugar is precipitated, this should be studied in more detail. It is an abnormal case though the author considers it the type case.

The author quotes Trautz, p. 64, to the effect that the first stage in the decomposition of ammonia is the formation of $NH + H_2$, and that the activation of nitrogen at low temperatures gives N_3. Since there is no ionization when nitric oxide, hydrobromic acid or hydrogen reacts with chlorine, the author concludes, p. 65, that activation consists only in a displacement of the valence electrons. Apparently, independent proof of such a hypothesis is not necessary. It is postulated also, p. 67, that all cases of contact catalysis involve the intermediate formation of a definite chemical compound between the catalytic agent and at least one of the reacting substances. It is admitted, p. 75, that the formation of nitrosyl chloride is a trimolecular reaction; but the author considers this so improbable that he advises ignoring it and treating the case as really two bimolecular reactions.

On p. 84 it is pointed out that if one saponifies methyl oxalate with ammonia, adding ammonium salts as a buffer, it is possible to show that the first methyl group is split off ten thousand times as rapidly as the second one. The author points out, p. 86, that the rate of inversion of cane sugar is not strictly proportional to the concentration of hydrogen as ion; but he comforts us by saying that we can account for the phenomena very satisfactorily if we take into account the activities of monohydrol, dihydrol, etc.; and the activities of the hydrogen ion, of the undissociated acid, the hydrated and unhydrated sugar, etc.

Even this is adequate only for this particular case. "It seems that the usual conception of ion catalysis is too schematic even when we substitute activities for concentrations. Most of the newer investigations on the mechanism of reactions indicate that more or less stable intermediate products are formed," p. 88.

Aniline appears quite hopeless as a solvent, p. 137. "In general the strong acids behave as though they were either completely associated in aniline or not at all. Weaker acids, such as the substituted benzoic acids do not catalyze the change of diamidoazobenzene into amidoazobenzene proportionally to their concentration, the rate increasing more rapidly than the concentration. Addition of water to the aniline decreases the rate when the acid is a strong one and accelerates it for a weak acid. Conductance experiments in aniline all gave the long-known peculiarity that the equivalent conductivity first decreases and then increases with increasing dilution."

Under photochemistry we are advised, p. 150, not to speak of light-sensitive systems; not single reacting components, but of complexes which these form with one another. The author is bothered, p. 158, that not all the substances which absorb light seem to be light-sensitive. He seems not to have read the papers of Grotthuss, whose name he mis-spells, and there seems to be no mention in the book of a photochemical depolarizer. There is also nothing to show what connection there is between reaction velocity and photochemical displacement of equilibrium. On p. 174 the author points out that we know that Einstein's application of the quantum theory to photochemistry must be a fundamental law because we can think up explanations for all the exceptions.

The book is not really such a caricature as these quotations imply. There are many pages which are quite commonplace.

Wilder D. Bancroft

Physico-Chemical Geology. *By R. H. Rastall. 22 × 14 cm; pp. vii + 248. London: Edward Arnold and Co. 1927. Price: 15 shillings.* The methods and conceptions of physical chemistry are fruitfully applied in the study of many geological problems, and have undoubtedly led to greater precision in the interpretation of available data. The conditions of solid-liquid equilibria, for example, as affected by temperature and pressure changes, may be rationally treated along the lines of the Phase Rule, and a considerable portion of the interesting volume under review is devoted to the phase relationships in systems of varying complexity. Among the matters set in the forefront of the author's treatment are such topics as:—the states of matter and the principle of equilibrium, fusion and solidification, isomorphism and solid solutions, polymorphism and inversions, physical chemistry of rock weathering and of igneous rocks, colloids, salt and ore deposits, refractories and abrasives. The author writes as a geologist and it is therefore not surprising that in some parts of the book the geology is more prominent than the physical chemistry. So far as the exposition deals with physico-chemical principles it is generally sound, although there is room for criticism here and there. Thus, for example, the liquidus curve in Fig. 15c is erroneously drawn as if it were characterised by an ordinary eutectic point: the statement that lead and tin when melted together in equal quantities separate into two layers is wrong: the curves in Fig. 40 are described as melting point curves, whereas they are vapour pressure curves: on p. 78 "morphotropy" is used instead of "monotropy."

In a discussion of the manner in which water is held by the crystalline zeolites it is stated that the amount of water in the zeolite is solely a function of the temperature: this requires correction, for the water held is also a function of the water vapour pressure in the surrounding atmosphere. Further, the author seems to suggest that while the dehydration of the zeolites is a completely reversible process, that of hydrated copper sulphate is in a different category. There appears to be some confusion here, for the dehydration of crystallised salts, although it takes place discontinuously, is none the less reversible.

The conceptions of reversibility and mass action, which have played such an important part in the physico-chemical treatment of equilibrium, receive somewhat scant attention in this volume. It is true that the author here and there employs the double arrow, but an adequate exposition of all that lies behind the use of this symbol would have been welcome. Greater emphasis too might have been laid on the significance of the Le Chatelier-Braun principle in connexion with purely chemical equilibria.

To write a book on physico-chemical geology which shall not be open to criticism from one side or the other is no easy matter, and if a similar attempt were made by a physical chemist instead of a geologist the hypothetical author would quite likely come to grief in his geology. It does seem to the reviewer, however, that if the MS. of the present volume had been submitted to a competent physical chemist many errors which have crept into the text would have been avoided. The presence of these detracts a little from what is, in general, a valuable introduction to a fascinating subject.

J. C. Philip.

DETERGENT ACTION OF SOAPS. II

BY GEORGE PAUL VINCENT

The truest measure of the detergent action of soaps is obtained by actual washing tests. An approximation may be obtained by other methods. Chief among these may be listed the ability of the soap solution to suspend a solid material stably and to carry solid material through a filter paper.

If the particles of a solid are sufficiently small, soap solution will prevent them from settling; and most of these same particles, which are stably suspended, will pass through the pores of a filter paper. The two methods should give comparative results.

It is not to be assumed that the particles which are too large to be suspended, or carried through filter paper, are not cleansed from fabrics and the skin by soap solution. There is no known means by which these larger particles of solid material can be fitted into a quantitative measurement of detergent action, but the smaller particles can be utilized in the manners described.

The convincing evidence, that detergent measurement by the stable suspension method gives dependable results, is found in the agreement of these results with those obtained in actual washing practice.

"Stabilized" material, as used throughout this paper, is that material in suspension, which does not settle when allowed to stand for a long period of time (arbitrarily 10 to 20 hours), and which will pass through the pores of a filter paper.

McBain,[1] by utilizing Spring's[2] discovery that soap solutions will carry carbon black through filter paper, has worked out a quantitative method for measuring the detergent power of soaps. From his extensive studies, he finds that the amount of carbon black carried through filter paper increases with increasing soap concentration up to a definite maximum, and from that point decreases. This maximum occurs at a soap concentration of 4.45 per cent. The conclusion is drawn, that a concentration of 4.45 per cent is the most efficient concentration of soap to employ in the detergent process.

Fall[3] undertook a study of the same problem some few years later. McBain's method was a bit erratic and at best was none too accurate. Fall succeeded in obtaining a means of measuring detergent action by a study of the extent of stabilization of MnO_2 in soap solutions. His method was free from many of the disturbing factors encountered by McBain and was consequently subject to a smaller percentage error. Fall's work indicated, as

[1] McBain, Harborne and King: J. Phys. Chem., **28**, 1 (1924).
[2] Kolloid-Z., **4**, 164; Rec. Trav. chim., **28**, 120 (1909).
[3] Fall: J. Phys. Chem., **31**, 801 (1927).

had McBain's, that the stabilizing power of any soap increases with its concentration up to a maximum. Increasing the soap concentration beyond this point causes a loss in stabilizing power.

The unfortunate thing in the two pieces of work was, that they did not exhibit this maximum at the same soap concentration, McBain finding it at 4.45 per cent, Fall at 0.2-0.4 per cent.

It is the purpose of this paper to attempt an explanation of the reason for obtaining such a maximum as above described, to correlate the work of McBain and Fall, to study the cleansing of oils as exemplifying liquid dirts, to determine the value of the common addition agents added to soaps, to explain the powerful detergent action of sodium phosphate toward specific greases, and to point out the reason for the beneficial effects obtained in the bleaching of fabrics by employing a bleaching solution containing sodium silicate.

Explanation of Maximum found by Fall

The theory for the explanation of the fact that Fall found one certain soap concentration which stabilized more MnO_2 than any other concentration is as follows:

The MnO_2 in stable suspension possesses a negative charge. This is the result of adsorption of negative oleate, palmitate, or other such ions in true solution, by the MnO_2. The MnO_2 also has the ability of adsorbing positive ions from solution. In dilute solutions the negative ion is adsorbed more strongly than the positive ion. But as the soap concentration is increased the adsorption of the positive ion is likewise increased. Eventually a concentration is reached where the positive ion is adsorbed to the same extent as the negative ion. At this point the MnO_2 possesses no charge and therefore no stable suspension results. The maximum suspension occurs at the soap concentration from which the negative ion is adsorbed the strongest in comparison to the adsorption of the positive ion. This state of affairs, as regards the adsorption of the two oppositely charged ions, must occur at a soap concentration of 0.2-0.4 per cent, for this concentration of soap will stabilize the greatest amount of MnO_2. In such extremely weak solutions the soap present is practically entirely in true solution,[1] so the charge is due to the adsorption of simple negative soap anions in true solution.

The possibility of molecularly dissolved, instead of colloidal soap, acting as a detergent has been pointed out by Chapin.[2]

Experimental

That a negative charge is possessed by the stabilized MnO_2 is shown by the following:

A suspension of MnO_2 in 0.4 per cent soap solution was subjected to a direct electrical current in a cataphoresis tube. The soap was palm oil, furnished by the Palmolive Company. The analysis of it is given in Fall's

[1] McBain: Bancroft's "Applied Colloid Chemistry," 305 (1926).
[2] Chapin: Ind. Eng. Chem., **17**, 1187 (1925); **18**, 1313 (1926).

paper.[1] The manganese dioxide was some of Fall's own supply—stock room manganese dioxide which had been milled very fine in the colloid mill of the Premier Mill Corporation of Geneva, New York. The cataphoresis tube was made of heavy glass in the shape of the familiar U. It contained a stop-cock on each arm very near the bottom. The MnO_2 suspension was placed in the portion of the tube between the stop-cocks. The cocks were then closed and the portion above them was washed out with water. Distilled water, containing a drop or two of 4.0 per cent soap solution, was then placed in the arms. Graphite electrodes were introduced into the arms and a 110-volt current was applied. The stop-cocks were opened. After a short interval of time it was plainly evident that the stabilized MnO_2 was negatively charged. It migrated very strikingly and completely to the anode. Many repetitions of the same experiment gave identical results.

This is excellent evidence that the MnO_2 is adsorbing the negative ion of the soap molecule.

Indication that the positive ion is also adsorbed is furnished by the next experiment.

If complete settling occurs because of adsorption of the positive ion of the soap molecule by the negatively charged MnO_2, adding some substance to the soap solution which supplies positive ions should cause this "no stabilization concentration" of the soap to be reached with less soap than if no substance were supplying the positive ions except the soap. This is obvious. The positive ions cause the settling. Ordinarily they come from the soap alone, and

TABLE I

No.	Per cent Soap	Addition Agent	Quality of Suspension
1	4.0	None	Good
2	"	5 c.c. 5% NaCl	"
3	5.0	None	Good
4	"	5 c.c. 5% NaCl	Not quite as good
5	5.5	None	Good
6	"	5 c.c. 5% NaCl	No suspension
7	5.5	None	Good
8	"	5 c.c. 5% NaCl	No suspension
9	6.0	None	No suspension
10	"	5 c.c. 5% NaCl	" "

[1] Fall: J. Phys. Chem., **31**, 801 (1927).

the concentration of the soap must be sufficiently great to supply the amount of positive ions needed. If they are partially supplied by some other agent less soap will be required.

One gram portions of the "milled" MnO_2 were shaken with 50 c.c. of olive oil soap solution in 100 c.c. oil sample bottles. The shaking was done by a machine through a period of four minutes. The suspensions were allowed to stand 24 hours and were then examined, Table I.

Two bottles of 5% soap solution were not treated with MnO_2. To one of these 5 c.c. of 5% NaCl were added. The shaking and length of standing were the same as the others shown in the table. The two solutions were examined at the end of 25 hours. The one which contained the NaCl was in no way inferior to the soap solution to which no salt had been added. This showed that sufficient salt solution had not been added in the above experiment to be detrimental to the soap in solution.

Discussion

The experiment indicates that the sodium ion is adsorbed and, thus, causes settling of the negative suspension. In bottles one and two there is not sufficient sodium ion present to cause settling. The same is true of bottle three. But bottle four shows a slight tendency to be inferior. Bottle five which contains 5.5% soap forms a good suspension with MnO_2. But in bottle six the sodium ion content is increased by the addition of NaCl to a concentration which causes complete settling. Seven and eight are checks on five and six. In nine and ten complete settling occurs, for at a soap concentration of 6% there are sufficient sodium ions present in the soap to cause settling without the addition of any NaCl.

McBain and Fall plotted soap concentration against stabilizing ability. Maxima occur in these curves. The above experiments agree with the theory postulated for the explanation of such maxima. They represent the soap concentrations at which the adsorption of the anion is strong and that of the cation is weak.

TABLE II

No.	Addition agent	Amount of Addition Agent added	Quality of Suspension
1	NaCl	1 c.c.	Good
2	KCl	"	"
3	NaCl	2 c.c.	Good
4	KCl	"	"
5	NaCl	3 c.c.	Good
6	KCl	"	No good
7	NaCl	4 c.c.	No good
8	KCl	"	" "
9	NaCl	5 c.c.	No good
10	KCl	"	" "

McBain found the most efficient soap concentration to be 4.45%, Fall 0.2-0.4%. There must be some reason for this discrepancy. One very possible solution was suggested by the fact that McBain's experiments were all performed with potassium soaps, whereas Fall used sodium soaps. If this were to account for the difference it would mean that the potassium ion is less strongly adsorbed than the sodium ion, thus necessitating a much higher soap concentration to cause settling. But by using an equimolecular KCl solution in place of the NaCl of the previous experiment, this was shown not to be the case. For when 1 gram of MnO_2 and equimolar NaCl and KCl was shaken 50 times with 25 c.c. of 5.5% olive oil soap at a temperature of 45°-50° C. and allowed to stand 16 hours the conditions obtain as given in Table II.

3 c.c. of KCl, No. 6, is sufficient to cause complete settling of the suspension whereas 4 c.c. of NaCl, No. 7, is necessary. This demonstrates that the potassium ion is adsorbed as strongly as the sodium ion. Any difference in the amount of adsorption is in favor of the potassium ion being adsorbed the stronger.

Evidently the explanation we are seeking is not to be found in the fact that one investigator used sodium soaps, while potassium soaps were employed by the other.

This was checked further by employing potassium oleate instead of sodium oleate in making suspensions of MnO_2. These suspensions, as regards settling, behaved in an exactly analogous manner to those in which sodium oleate was used. Complete settling occurred with 50 c.c. of soap solution and 1 gram of MnO_2 at a soap concentration of 6-7% in each case.

Correlation of the Results of McBain and Fall

After some further preliminary work it was found that, if the suspensions being filtered contained coarse, non-stabilized carbon, this carbon would clog the filter, so that the fine, stabilized carbon could not pass through.

McBain's experiments were subject to this error. Any change in the experimental procedure which prevents the coarse carbon from interfering with the filtration of the fine material, causes the experiments of McBain to agree with those of Fall.

The following experiments corroborate the above statements:

Experimental

The potassium oleate used was precipitated with the calculated amount of KOH from U. S. P. oleic acid, and diluted to the strength desired by means of the formula given by Bunbury and Martin.[1] Soap prepared in a like manner from Kahlbaum's pure oleic acid, or potassium oleate prepared by Kahlbaum, acted in a similar manner to the soap prepared from the U. S. P. oleic acid.

In the experiments to follow, potassium oleate was always used unless stated differently.

The carbon was of two varieties. One type was Kahlbaum's refined bone charcoal, which was washed with cold and hot water until the washings

[1] Bunbury and Martin: J. Chem. Soc., **105**, 417 (1914).

showed no cloudiness with $AgNO_3$. The other variety was carbon similar to that just mentioned, except that it was further disintegrated by passing it through the colloid mill of the Premier Mill Corporation of Geneva, New York.

The containers were 100 c.c. oil sample bottles unless otherwise noted. The agitation was done by hand. The carbon which had not been run through the colloidal mill is labeled "Ordinary," that which had been so treated is labeled "Milled." Room temperature was always employed unless stated differently.

In all of the following experiments the 0.4% soap solutions contain more stabilized carbon than the 4.45% solutions, (Fall's results) but this is not apparent in every case. The purpose of these experiments is to explain what masks this truth.

The fact, that coarse, non-stabilized carbon will prevent the fine material from passing through filter paper is demonstrated by the following two experiments:

No. 1. 1 gram of milled carbon was shaken 100 times with 50 c.c. of a 0.4% potassium oleate solution. After standing for a period of time (this bottle happened to stand 42 hours) a portion was removed with a 10 c.c. pipette. This filtered very black. A similar portion was filtered through a paper, which had been previously prepared by pouring upon it a water suspension of milled carbon. This filtrate came through practically colorless.

This demonstrates that the non-stabilized carbon interferes with the passage of the stabilized carbon through the paper.

No. 2. The following solutions were filtered before the coarse carbon could settle away from the fine material in suspension. These solutions containing 1 gram of carbon were shaken 100 times and immediately filtered upon 12.5 cms. filter papers. 5 c.c. of the filtrate were collected in graduated cylinders and were examined, Table III.

TABLE III

No.	% Soap	c.c. Soap Solution	Nature of Carbon	Color of Filtrate
1	4.5	20	Ordinary	The filtrates were so devoid of carbon that to attempt any differentiation would be foolish.
2	0.4	20	"	
3	4.5	20	Milled	
4	0.4	20	"	
5	4.5	50	"	
6	0.4	50	"	

This experiment indicates that the coarse material clogs the filter paper so that the fine carbon can not pass through.

McBain shook one gram of carbon black with 20 c.c. of soap solution, allowed this to stand for 23 hours, shook again, let stand one more hour, and then poured the entire liquid upon a filter paper. He collected a definite

amount of filtrate, and from the amount of carbon present calculated the "carbon number" of the soap solution.

With this method the non-stabilized material is given only one hour to settle before filtering. Consequently, when the solutions are filtered, much non-stabilized carbon is poured on the filter paper.

McBain's 4.45% soap solution filtrate contained much more carbon than the 0.4%. This is because the coarse carbon in the 4.45% solution settles more rapidly than in the 0.4% solution. Thus, upon filtering it cannot clog the pores of the paper and the fine particles can pass through. But the slow settling of the coarse material in the 0.4% solution allows much coarse carbon to be poured on the paper with the fine material. The pores become clogged and the fine material cannot filter.

The reason for the difference in the rates of settling is probably a factor of the stabilized carbon present. The 0.4% solution contains a large amount of fine, stabilized material, so much in fact that it is difficult for the coarse material to settle through it. The 4.45% solution contains less stabilized carbon, and consequently the coarse material settles more rapidly as it encounters no impediments in its downward path.

Reasoning in this manner it might be assumed, that if the solutions were allowed to stand a very long time before filtering, the 0.4% soap filtrate should contain more carbon than the 4.45%.

1 gram of milled carbon was shaken 100 times with 20 c.c. of potassium oleate solution. The solutions were allowed to stand the number of hours indicated. 10 c.c. were then pipetted off and filtered, Table IV.

TABLE IV

No.	% Soap in solution	Time	Color of Filtrate
1	4.0	16 hours	Very dark
2	0.4	" "	Almost colorless
3	4.0	50 "	To eye the same. In colorimeter (3) just slightly darker.
4	0.4	" "	
5	4.0	74 hours	To eye the same. Colorimeter showed (5) 1.3 times darker than (6)
6	0.4	" "	

This experiment did not yield as satisfactory results as desired. But it shows that, up to a certain point, as the time allowed for settling is increased, the 0.4% filtrate becomes darker in respect to the 4.45% filtrate. Increasing the settling time beyond this point (50 hours) yields no better results.

The soap-carbon ratio is of great influence upon the color of the filtrate obtained, Table V. 20 c.c. of potassium oleate were employed at room temperature.

TABLE V

No.	% Soap in Solution	Nature of Carbon	Grams Carbon	Treatment	Color of Filtrate
1	4.5	Ordinary	1	Shaken 100 times. Stood 16 hrs. Poured on filter. 5 c.c. collected.	Slightly darker than (2)
2	0.4	Ordinary	1	"	Slightly lighter than (1)
3	4.5	"	2/5	"	Lighter than (4)
4	0.4	"	"	"	Darker than (3)
5	4.5	Milled	1	"	Very dark
6	0.4	"	1	"	Almost colorless
7	4.5	"	2/5	"	Dark. Less than (8)
8	0.4	"	1	"	Very dark

It is seen that when 1 gram of carbon and 20 c.c. of soap solution are used, allowing settling to occur and then filtering, the 4.5% soap filtrate contains more carbon than the 0.4%. But when only 2/5 of a gram of carbon is used with 20 c.c. of soap solution (this is equivalent to 1 gram of carbon with 50 c.c.) the 0.4% soap filtrate contains vastly more carbon than the 4.45%.

In other words, increasing the volume of soap solution to 50 c.c. causes the experiments to behave in accordance with Fall's results. This is attributed to the greater ease with which the coarse carbon can settle in the solutions containing a lower concentration of total solids. It may very well be considered as the reverse of consolidation and subsidence settling of ore pulps. "If there is a large amount of water present and the pulps are consequently very dilute, each particle separates practically unaffected by the others. . . . with increasing concentration the coarser particles tend to interfere with the finer ones and to carry them down. . . . the higher concentration giving what Free calls consolidation settling and the lower concentration subsidence settling."[1]

For our purposes we postulate that when the solutions are very concentrated in respect to carbon, the large number of finer particles tend to interfere with the coarser ones and to hold them up.

With both 20 c.c. and 50 c.c. of soap solution the 0.4% concentration has more fine particles of carbon suspended than the 4.45%. Consequently the influence of the fine particles on the coarser particles is greater in the 0.4%

[1] Bancroft: "Applied Colloid Chemistry," 234 (1926).

solution. With 20 c.c. of 0.4% soap solution this influence is so great that only a slight amount of coarse carbon settles, and consequently only a small amount of fine carbon can pass through the clogged pores of the paper. This influence is less marked with the 4.45% solution and therefore this filtrate contains more carbon than the 0.4%. But when 50 c.c. of soap solution are employed the concentration of fine carbon per c.c. is so greatly reduced, that the coarse carbon settles as it should even in the 0.4% solution. Then upon filtering, the 0.4% solution contains more carbon than the 4.45%.

One other factor which entered into McBain's experiments, and which bears directly upon the clogging of the paper by the coarse particles of carbon, is the time element.

It will be remembered that McBain's solutions were allowed to stand 23 hours after the initial shaking, were then shaken again, allowed to stand for one hour, and were then filtered.

When coarse, non-stabilized carbon has been in contact with a 4.45% soap solution for a considerable time, it has lost much of its ability to clog the pores of the paper. The following experiments illustrate this.

No. 1 1 gram of "ordinary" carbon was shaken 100 times with 20 c.c. of 4% soap solution. After standing 118 hours the solution was again shaken 100 times and immediately filtered. After filtering, the filter paper was covered of course with non-stabilized carbon which had been in contact with soap solution for a long period of time.

A carbon suspension was formed by shaking 1 gram of "ordinary" carbon with 50 c.c. of 0.4% soap solution. This was allowed to stand for 24 hours, 10 c.c. were then pipetted from the supernatant liquid and were filtered through the paper prepared as mentioned above. 5 c.c. were collected.

The filtrate possessed a decided black color.

The same effect can be produced by heating the 4.45% suspension.

No. 2 1 gram of "milled" carbon and 20 cc. of 4.45% potassium oleate solution were held at a temperature of 90–95° C. for 20 minutes. The solution was then shaken 100 times and filtered immediately. 5c.c. of the filtrate were collected. The color of this filtrate was very dark. It will be remembered that a solution treated similarly, except that no heat was applied, filtered practically colorless.

This behavior is attributed to the hypothetical ability of concentrated soap solutions to agglomerate the coarse carbon into such large particles that they do not clog the filter paper pores. This agglomeration presumably occurs slowly, and for this reason is facilitated by time and heat.

As McBain's solutions were so treated that this time effect came into play, the 4.45% solutions filtered much darker than the 0.4% solutions.

Another indication of the interference by non-stabilized carbon is apparent from a study of "ordinary" carbon. At a soap concentration of 4.0% the "ordinary" carbon suspensions are entirely free from suspended material if allowed to stand over night. If, however, a solution which has stood over night is now shaken again and allowed to stand, a portion of the carbon is

stably suspended. Or if the mix of soap and carbon is heated before the first shaking, it will then form a stable suspension. This is corroborated by Table VI.

TABLE VI

No.	% Soap	c.c. Soap Sol.	Nature of carbon	Gr. carbon	1st Treatment	Suspension	2nd Treatment	Suspension
1	4.0	20	Ordinary	1	Shaken 100 times Stand 16 hours	None	100 more shakes. Stand 24 hours	Good
2	4.0	20	"	1	Held at 90°C. for 20 min. 100 shakes Stood 23 hours.	Good	—	—

Suspensions are formed with milled carbon upon the first shaking and without employing elevated temperatures.

These facts probably can be accounted for as follows: With the ordinary carbon at a soap concentration of 4.0% there is present only a small amount of fine stabilized particles. Consolidation[1] settling works in the ordinary manner. "The coarser particles tend to interfere with the finer ones and to carry them down." But after the solution has been so treated that the coarse, non-stabilized particles are aggolomerated into only a few relatively large particles, subsidence settling occurs "and each particle separates practically unaffected by the others."

In such a process the fine, stabilized particles are not agglomerated, probably because of their relatively large electric charge in comparison to their mass.

With milled carbon there are so many fine, stabilized particles present that the coarse ones cannot drag them all down.

As final evidence that the 0.4% soap solution does contain more stabilized carbon than the 4% solution, the following is offered: Suspensions containing 1 gram of milled carbon in 20 c.c. of 4% and 0.4% potassium oleate were made by shaking 100 times. After standing 15 hours a portion of each suspension was removed by means of a pipette and subjected to cataphoresis. A 110 volt current and carbon electrodes were employed. At the end of 10 minutes the suspension formed with the 0.4% soap solution had migrated 1 cm. toward the anode. The migration was very rapid and very definite. When the suspension, which had been formed with the 4.0% soap solution, was treated in a similar manner scarcely any migration had occurred at the end of six hours.

[1] Bancroft: "Applied Colloid Chemistry," 234 (1926).

This shows definitely that the charge on the carbon in a 0.4% solution vastly greater than when a 4% soap solution is used. As the charge is stronger, and as the amount of material stabilized must depend on the charge (i. e. the amount of negative ions adsorbed by the carbon) there is no alternative to the fact, that the 0.4% solution contains more stabilized carbon than the 4%.

In point of digression it might be said, that possibly a quantitative method for the extent of stabilization could be found by measuring the rapidity of the movement of the suspension under electrical stress.

From the work here cited, it is plainly evident that McBain's[1] results were correct for the conditions which he employed. But the purpose of his investigation was to find the soap concentration at which the greatest amount of carbon is stabilized. In this he failed. Fall's[2] determinations, which show that .2–4.% soap causes the greatest stabilization, stand uncontested.

By regulating McBain's experiments so that the coarse, non-stabilized carbon does not interfere in the settling process, and subsequent filtration, his results can be made to agree with those obtained by Fall.

Emulsification Investigation

As Fall[3] has made an extensive study of the detergent action of soap and other substances upon solid dirts, the purpose of the following investigation was to carry this work into the field of the liquid dirts.

Oils, greases, and fats are supposed to be removed in the cleansing process by emulsification. By learning the detergent, concentration, and temperature which cause the best emulsification, considerable information should be gained as to the most beneficial conditions to employ in washing.

In order to ascertain these conditions the following work was performed.

Experimental

Due to the fact that kerosene oil is a typical example, easy to work with, and inexpensive, it was selected as the liquid dirt with which to perform the majority of the experiments.

TABLE VII

Per cent and brand of soap	Quality of Emulsion	
	At start	16½ hours later
Palm oil		
1.00	Emulsified	Good
0.50	"	"
0.25	"	"
0.10	"	"
0.05	"	Good. Very slight amount oil on top
0.01	"	No good

[1] McBain, Harborne and King: J. Phys. Chem., **28**, 1 (1924).
[2] Fall: J. Phys. Chem., **31**, 801 (1927).
[3] Fall: J. Phys. Chem., **31**, 801 (1927).

TABLE VII (Cont.)

Per cent and brand of soap	Quality of Emulsion: At start	Quality of Emulsion: 16½ hours later
Olive oil		
1.00	Emulsified	Good
0.50	"	"
0.25	"	"
0.10	"	"
0.05	"	Good. Very slight amount oil on top
0.01	"	No good
Green Arrow		
1.00	Emulsified	Good
0.05	"	"
0.25	"	"
0.10	"	"
0.05	"	Good. Very slight amount oil on top
0.01	No emulsion	No good
Silicated Green Arrow		
1.00	Emulsified	Good
0.50	"	"
0.25	"	"
0.10	"	"
0.05	"	Good. Very slight amount oil on top
0.01	"	No good
Tallow		
1.00	Emulsified	Good
0.50	"	"
0.25	"	"
0.10	"	"
0.05	No emulsion	No good
0.05	Emulsified	Good. Very slight amount oil on top
0.05	"	"
0.05	"	"
0.01	No emulsion	No good

The emulsions were made in 100 c.c. oil sample bottles, by hand shaking 20 consecutive times 25 c.c. of soap solution of the indicated strength and 25 c.c. of kerosene oil. The temperature was 40° C. The concentration of the soap was figured on a moisture free basis. The results are given in Table VII.

These five commercial soaps, Palm Oil, Olive Oil, Green Arrow, Silicated Green Arrow, and Tallow were furnished by the Palmolive Company. Their analyses are given by Fall.[1]

These data show that all five soaps possess practically identical emulsifying powers, and that the necessary soap concentration to assure emulsification upon a minimum of agitation is from 0.05 to 0.10 per cent.

To make certain that the amount and nature of the oil do not greatly influence the soap concentration necessary to cause emulsification, a smaller amount of kerosene, and a heavier oil, were subjected to emulsification tests, Table VIII.

The conditions under which the experiment was performed were the same as those employed in the previous experiment, except for the changes noted in the amount and nature of the oil. The heavy oil was a viscous machine oil.

TABLE VIII

Palm Oil Soap

Per cent Soap	c.c. Oil	Nature of oil	Observations	
			4½ hours after shaking	19¾ hours after shaking
0.250	2.5	Kerosene	Good	Good
0.100	"	"	"	"
0.050	"	"	"	Good. Very small am't excess oil
0.010	"	"	"	Good. Small am't excess oil
0.005	"	"	No good	No good
0.500	2.5	Heavy	None com	Good
0.250	"	"	pletely	"
0.100	"	"	emulsified	"
0.050	"	"	but these 4 emulsified to about same extent	Nearly as good as first three
0.010	"	"	No good	No good

This table shows that employing a smaller amount of oil lowers slightly the soap concentration that must be used to cause emulsification. The concentration necessary to emulsify the heavy oil is not vastly different from that needed for kerosene.

[1] Fall: J. Phys. Chem., **31**, 801 (1927).

The effect of temperature was investigated, Table IX. The emulsions were made, as before, in 100 c.c. oil sample bottles which contained 25 c.c. of soap solution of the indicated concentration and kerosene oil of the quantity designated. The bottles were shaken 20 times by hand. The emulsions were formed at 80° C., and allowed to stand at 45° C. Olive oil was the soap employed.

TABLE IX

Olive Oil Soap

Per cent Soap	c.c. Kerosene	Observations At start	16¾ hours later
0.50	25.0	Good	Good
0.50	"	"	"
0.25	"	"	"
0.25	"	"	"
0.10	"	"	Good. Some breakage bubbles.
0.10	"	"	Good. Some breakage bubbles.
0.05	"	No good	No good
0.05	"	" "	" "
0.25	2.5	Amount	Good
0.25	"	oil too	"
0.10	"	small to	"
0.10	"	judge	"
0.05	"	extent	Good. Slight excess oil
0.05	"	emulsi-	" " " "
0.01	"	fied at	No good
0.01	"	start	" "

The same relative values were found to hold for the other four brands of soap.

At this elevated temperature the necessary soap concentration to cause emulsification is raised in the case of 25 c.c. of kerosene, from 0.05–0.10% to 0.10–0.25%, and with 2.5 c.c. oil, from 0.01–0.05% to 0.05–0.10%.

Similar experiments using the heavy machine oil showed an increase in temperature to be detrimental to emulsification.

Emulsification would take place at room temperature with less soap than is required at 40° C., but here the viscosities of the solutions are so high, that intimate mixing of the kerosene and soap solution is retarded to such an extent as to be detrimental.

Experiments performed with 10% Olive Oil, and 5% Olive Oil and Tallow soaps showed that high soap concentrations are not conducive to poor emulsification. Fall found such concentrations entirely unable to suspend solid material.

Discussion.

The foregoing work points out that all five soaps employed are of equal value in the emulsification of oil by water. The only possible discrepancy being exhibited by the Tallow soap which occasionally was very slightly inferior.

A soap concentration of 0.05–0.10% is amply sufficient, this concentration giving good emulsification with an amount of kerosene equal to the amount of soap solution used, and emulsifying well a heavy machine oil. With only 10% kerosene as compared to the volume of soap solution, a concentration of 0.01–0.05% is sufficient. This latter amount of kerosene is much closer to the proportion of oil that would be found in actual washing practice, than is the former amount of 50%. Thus, a soap concentration of 0.05–0.10% offers a margin of safety.

The probable reason for the deleterious effect of high temperature upon emulsification is to be found in the following quotation from Bancroft.[1] "In making emulsions of oil in water by means of sodium oleate, it must be remembered that the soap does not go entirely into the interface. There is always a relation between the concentration of the soap in the interface and the amount still peptized in the water. It is a case of the distribution of soap between the water and the interface. Anything that cuts down the peptizing action of the water on the soap will increase the amount going into the interface, and anything increasing the peptizing action of the water will decrease the amount of soap in the interface. It is not a question of osmotic pressure or of solubility."

When the temperature of the soap solution is raised the peptizing action of the water is increased, and consequently the amount of soap in the interface is decreased. This decreases the emulsifying power of the soap solution.

At emperature of about 40° C., (104° F.,) is recommended. At this point the solution is sufficiently hot to dissolve the soap readily, and the viscosity is low enough so that it does not interfere with the easy mixing of the oil and soap solution, and the temperature is not so high as to require a large amount of soap to cause emulsification. Also, as Fall has shown, the lower the temperature that can conveniently be employed the greater will be the amount of solid material suspended.

The Effect of Addition Agents upon Emulsification

Alkaline salts aid emulsification. Sodium carbonate and borax do not seem as efficient as do sodium phosphate, sodium hydroxide, and ammonium hydroxide. The sodium hydroxide and sodium phosphate must not be used in too concentrated a form or they become detrimental. The ammonium hydroxide can be used in any amount. This is probably due to its much weaker hydroxyl ion content. The emulsions formed with the aid of NH_4OH were more permanent than those stabilized by any other addition agent studied.

A solution 0.32% in respect to sodium hydroxide is sufficiently concentrated to aid and not concentrated enough to be detrimental to emulsification.

[1] Bancroft: "Applied Colloid Chemistry, 357 (1926).

When ammonium hydroxide is used, the washing solution should contain 1.2 per cent or more NH_4OH, or figured on an NH_3 basis, 0.65 per cent or more of NH_3.

The reason that these alkaline substances exert a beneficial influence upon emulsification, is undoubtedly due to the fact that they lower the surface tension of water toward the oil in the presence of a soap solution. This has been demonstrated with benzene by Harkins and Zollman.[1]

Sodium Silicate as an Emulsifying Agent

Fall[2] has shown that sodium silicate will peptize solid dirts practically as well as will olive oil soap, and 80–88% as efficiently as will the other four soaps used. Stericker[3] states that sodium silicate will emulsify oils to some extent.

If then silicate has the ability to cleanse from material both solid and liquid dirts, it should be possible to use it as a detergent to a much greater extent than is in vogue at present. However, the extent of the emulsification obtained by Stericker was very meagre, and to make certain of the value of sodium silicate as an emulsifying material the topic was investigated.

Experimental

Silicates were used of the composition given in Table X.

TABLE X

Brand	Per cent H_2O	Per cent Na_2O	Per cent SiO_2	Mol Ratio Na_2O: SiO_2
"C"	46.1	18.0	35.9	1 : 2.05
"U"	53.4	13.7	32.9	1 : 2.48
"O"	60.4	9.3	30.3	1 : 3.05

25 c.c. of kerosene were shaken in 100 c.c. oil sample bottles with 25 c.c. of "O" brand silicate. The concentration of the silicate was systematically varied over a range of 40.0% to 0.0002%. The bottles were shaken 20 times at room temperature. The same experiments were repeated using 2.5 c.c. of oil. No evidence of emulsification was apparent in either case. The experiments were repeated at 40° C. with the same results.

Then shaking intermittently for a considerable time at 40° C. was tried with 25 c.c. and 2.5 c.c. of kerosene. In no case was an emulsion worthy of note effected.

"U" and "C" brand silicates were studied at concentrations of 1.0–0.01%, with 2.5 c.c. and 25.0 c.c. of kerosene, at room temperature and at 40° C. No emulsification of any value occurred.

It has been shown that NH_4OH is beneficial to the emulsification process. For this reason the effect on the emulsifying process of sodium silicate by the addition of NH_4OH was investigated.

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[1] Harkins and Zollman: J. Am. Chem. Soc., **48**, 69 (1926).
[2] Fall: J. Phys. Chem., **31**, 801 (1927).
[3] Stericker: J. Ind. Eng. Chem., **15**, 244 (1923).

"O" brand silicate in 25 c.c. portions, of concentrations from 3.9 to 0.001 per cent was used. The dilute NH_4OH was 1/20 the strength of ordinary concentrated ammonia which is 23.68% NH_3, thus making the solution about 1% in respect to NH_3. 25 c.c. of kerosene were employed. The NH_4OH was added in the following amounts, after each addition the solution was shaken twenty times: 2 c.c. dilute, 2 c.c. dilute, 1 c.c. concentrated, and 5 c.c. concentrated. No emulsification occurred.

25 c.c. of 0.001 per cent silicate were shaken with 2.5 c.c. of kerosene and 7.0 c.c. of concentrated NH_4OH. No emulsification was evident.

Discussion

It is plainly seen that sodium silicate possesses no value whatsoever as an emulsifier of oils. Close examination of Stericker's results show that in all probability the oils which he used were slightly contaminated with fatty acids. These acids reacted with the silicate forming a soap which did the emulsifying.

"Wetting" as a Detergent Factor

Two important properties of a detergent have been discussed, viz: peptizing and emulsifying power. A third, and heretofore little noticed, property remains for consideration. This property is the "wetting" ability of the detergent.

It has been known for some time that sodium phosphate possesses considerable value as a cleansing solution. Trisodium phosphate is a constituent of many soapless washing powders, and some people claim that trisodium phosphate alone cleans overalls, which have been in use around automobiles, as nothing else will.

The reason for this detergent power of sodium phosphate was investigated. The first procedure was to determine if the phosphate possessed any emulsifying power toward oils. The results of this work showed the phosphate to possess emulsifying ability for some greases and not for others. But it will cleanse from fabrics and the skin greases which it will not emulsify. This property is due to the alkaline phosphate solution's ability to wet the oil and grease. It forms a thin layer between the fabric, or the skin, and the oil. The oil is then no longer held by the material to be cleansed and it floats away from it. Any alkaline salt, be it phosphate or not, possesses this property. It is simply a question of adsorption: the detergent's ability to squeeze in between the junction of the oil and the cloth, or skin.

Emulsification is beneficial but not absolutely necessary.

Experimental

The possibility of a calcium soap being present in the oils made an investigation of emulsification necessary. A reaction between this and the phosphate, producing a sodium soap and insoluble calcium phosphate, might have been responsible for the detergent action of the phosphate.

25 c.c. of kerosene were shaken 60 times in 100 c.c. oil sample bottles with varying concentrations of Na_3PO_4, Na_2HPO_4, NaOH, and sodium silicate. The concentration of the Na_3PO_4 and Na_2HPO_4 ranged from 14.0–0.01%,

the NaOH from 20.0–0.15%, and the sodium silicate from 40.0–0.04%, each bottle containing just one-half the concentration present in the previous one. A heavier oil than kerosene was also tried. This was a lubricating oil made by the Deyo Oil Co. Inc., and had a viscosity number of 500. 2.5 c.c. with 25 c.c. of soap solution were used.

No emulsification was apparent in any case. But the striking thing about these solutions is that they will remove from fabrics and the skin the oils which they will not emulsify. The cleansing ability of these compounds is not as great as that exhibited by the emulsifying agent, soap, but it is nevertheless present to a decided extent. About 30 c.c. of 0.12%, or 6 c.c. of 10% Na_3PO_4, will wash the hands free of kerosene.

The heavy oil was removed from the hands with Na_3PO_4, NaOH, Na_2CO_3, and sodium silicate. The ease with which the operation was accomplished was roughly proportional to the basicity of the solution.

Strips of unbleached muslin were soaked in this heavy machine oil. 1% olive oil soap solution removed the oil with ease. 10% Na_3PO_4 removed most of the oil after several treatments. 10% NaOH completely removed all odor of oil.

These solutions, which remove oils without emulsification, have one thing in common, they all "wet" the oil. This property is assumed to be due to the alkaline nature of the solution. Solutions which do not wet the oil, such as NaCl and other neutral and acid salts, are not able to remove oils.

Measuring Wetting Ability

Two methods have been found satisfactory for determining if a certain solution will wet an oil, and therefore if it is of any use as a detergent for oils.

The first of these consists of simply taking a cloth of some definite size, soaking it in the oil, and then placing it in the solution to be tested. At first it will float. The cloth is forced beneath the surface of the solution by means of a glass rod. Unless the solution is extremely highly adsorbed, the cloth will immediately rise so that it again floats upon the top of the solution. This process is repeated until the upper surface of the cloth remains submerged. This will yield rather fair quantitative, as well as qualitative results.

Such a method applied to unbleached muslin strips, 2 8/10 cm. by 3 1/10 cm., with heavy machine oil, gave the results in Table XI.

TABLE XI

Solution	Concentration	No. of submersions
Na_3PO_4	M/6	4
"	"	6
"	"	9
"	"	8
NaOH	"	6
"	"	7
"	"	5
"	20%	2
"	"	1
NaCl	10%	50 times had no effect

Equimolar solutions of Na_3PO_4 and NaOH possess about the same hydroxyl ion concentration. The table shows that Na_3PO_4 and NaOH of the same molar concentration possess nearly the same ability to wet oil. It also indicates that as the strength of the solution is increased, the wetting power likewise rises. Because of this it is assumed that the wetting power of the solutions is due to their alkaline nature. But the excellent wetting ability of soap cannot be accounted for in the same way.

Another method for determining the wetting ability of a solution toward oils is as follows: A cork is placed loosely in the bottom of a 5 m.m. tube 14 cm. long. This is inverted in the solution to be tested. Suction is applied with the mouth until the solution is within about 4 cm. of the top. The cork is then firmly pressed in place by exerting a slight pressure against the bottom of the beaker containing the solution. The tube is filled the remaining distance with oil by means of a medicine dropper. The open end is then closed with a cork which has been dipped into water. This latter precaution is to keep the oil from adhering to the cork. The tube is then inverted, which causes the oil to be on the bottom. If the solution is capable of wetting the oil, the oil will rise to the top. If, however, the solution cannot wet the oil, the repulsive force is sufficient to overcome the force of gravity and the light oil remains beneath the heavier solution. Air must be excluded or the oil rises with the bubble.

The oil rises when solutions of Na_3PO_4 and NaOH are employed, but refuses to do so when water, sodium chloride, and sodium acetate are used.

It was hoped that the time required for the oil to rise would provide a means for determining quantitative wetting measurements. Such was not the case.

The foregoing work on wetting as a factor in detergency, points out that substances which do not emulsify may have some value in the detergent process. Compounds such as Na_3PO_4, Na_2CO_3, and sodium silicate which have been considered nothing but adulterants when added to soap, are seen to possess cleansing ability.

Solutions which will emulsify oils are the best detergents for these oils. Emulsification might be considered loosely as the superlative case of wetting. When solutions do not emulsify but do wet the oils, they may be considered not as useless in their detergent effect, but as rather less effective than if they did cause emulsification. Wetting is one degree beneath emulsification in the detergent scale.

The ability of a solution to wet oil, and undoubtedly to wet solid material, is not lessened but is rather increased with increasing detergent concentration. Emulsification acts in a similar manner. It is undoubtedly due to this that good cleansing action occurs in concentrated soap solutions. Considered only from the point of view of peptization, this is not to be expected. It must be remembered that at least three things are important in the detergent process, peptization, emulsification, and wetting. Undoubtedly the most efficient solution, per gram of soap, to use is that solution in which the peptizing power of the soap is greatest. This does not mean that cleansing will

not occur at the higher soap concentrations, where the peptizing ability of the soap is absent. At such concentrations the cleansing process proceeds very nicely, due to the emulsifying and wetting powers of such solutions.

This wetting business has been very interesting, but as yet the reason for Na_3PO_4 seemingly being more effective than soap upon some greases has not been explained. This will be discussed next.

The Effectiveness of Na_3PO_4 and NaOH as Detergents for Greases containing Calcium Soaps or Saponifiable Matter

The wetting ability of Na_3PO_4 explains why it is able to cleanse to some extent oils and greases, but it does not explain why it is supposed to work better than soap itself upon garments which have been soiled at gasoline filling stations.

The immediate guess for the solution of the problem is that the greases contain calcium soaps which react with the alkali added and yield a water-soluble soap, this latter doing most of the actual cleansing.

It will be recalled that when kerosene or a heavy mineral oil was employed, no emulsification resulted with Na_3PO_4. Heavy greases are usually made by emulsifying water in oil by means of calcium soap. Such a grease should yield an emulsion when treated with an alkali. The following experiment demonstrates this:

The grease used was a heavy cup grease, not an oil. It was made by the Deyo Oil Co., Inc., whose products are sold under the trade name Galtex. A small amount of the grease was placed in 100 c.c. oil sample bottles and was shaken 100 times with 25 c.c. of detergent solution at a temperature of 60° C., Table XIII.

TABLE XIII

No.	Detergent	% Detergent	Quality of Emulsion
1	Na_3PO_4	M/2	All emulsified
2	"	M/4	Not quite all
3	"	M/8	" " "
4	NaOH	M/1	Best of last 4, but not very good.
5	"	M/2	No good
6	"	M/4	" "
7	"	M/6	" "

Emulsification occurred. Na_3PO_4 seemed more effective than NaOH.

Actual washing experiments corroborated the above results. Two pieces of unbleached muslin cloths, 4 × 5 cm., were treated with this grease. One was then stirred 4 minutes in M/2 Na_3PO_4 and the other in M/2 NaOH at a temperature of 60°–70°C. The cloths were then rinsed three times with hot water.

The one which had been in the Na_3PO_4 solution was clean. It possessed neither an oily odor nor a yellow color. But the cloth which had been subjected to the NaOH solution still had an odor of oil and possessed a yellow color. It was not clean.

There is no doubt of the effectiveness of Na_3PO_4 upon certain types of greases. It is even more effective than NaOH. The reason for this is made clear upon further study. The grease employed in the above experiment was subjected to a spectroscopical examination and, as was expected, was found to contain an extremely high percentage of calcium and a trace of magnesium. Beyond all doubt this calcium was present as a calcium soap, used as the emulsifying agent in forming the grease. When the phosphate is added, this immediately reacts to form sodium soap and calcium phosphate. This reaction yields the soap necessary to form emulsification, while at the same time it breaks down the grease. Both occurrences are of value in the detergent process. And just as Cofman[1] has pointed out that spontaneous emulsification may be caused from the energy liberated when a free fatty acid and an alkali unite, here the energy liberated, when the calcium soap and alkali unite, may be of value. This, however, is aside from the point and not at all necessary.

The reason that the NaOH is not as effective as Na_3PO_4 is due to the fact that $Ca(OH)_2$ is more soluble than $Ca_3(PO_4)_2$. When the calcium soap reacts with NaOH, sodium soap and $Ca(OH)_2$ are formed. When this reaction occurs with Na_3PO_4, sodium soap and calcium phosphate result. $Ca(OH)_2$ is soluble 0.17 parts in 100 of water at zero, and .08 at 100° C. $Ca_3(PO_4)_2$ is soluble .0023–.0031 parts in 100 of cold water, and it decomposes when hot. So even though both salts are relatively insoluble, $Ca(OH)_2$ is almost 100 times more soluble than $Ca_3(PO_4)_2$. Of course the more insoluble the reaction products are, the nearer the reaction will proceed to completion.

That the above explanation is correct is borne out in actual experimental procedure by the following: 10 c.c. of NaOH, of concentration ranging from 6.25 to 0.02 molar, were shaken with a small amount of calcium oleate 125 times, at room temperature. The amount of foam formed was very small.

The same experiment was repeated with Na_3PO_4 in concentrations from 0.657 to .02 molar. Copious foam was formed at concentrations from .657 to and including .082 molar.

0.5 molar NaOH and Na_3PO_4, with calcium oleate, were tried at 100° C. The NaOH solution had very little foam, whereas the Na_3PO_4 solution contained foam 5 cm. high in the bottle.

This demonstrates that the amount of sodium soap formed when calcium soap reacts with Na_3PO_4, is much greater than when calcium soap reacts with sodium hydroxide.

For a grease containing calcium soap, Na_3PO_4 is more effective than sodium hydroxide. And it is probably more effective than soap alone because calcium oleate tends to emulsify water in oil. In this respect it works in opposition to soap. Thus, its removal through chemical reaction, especially by means of a reaction forming sodium soap, is of utmost benefit to the cleansing process. But there is another grease in use, which yields results

[1] Cofman: E. I. du Pont de Nemours & Co., Unpublished Work.

quite similar with NaOH and Na_3PO_4. This is a viscous, black transmission liquid manufactured by the Deyo Oil Co. Its behavior with the two compounds is shown in the table below.

25 c.c. of the detergent were shaken 50 times with 5 c.c. of the oil in oil sample bottles, at a temperature of 60° C., Table XIII.

TABLE XIII

No.	Detergent	Molality of Detergent	Approx. % of Detergent	Quality of Emulsion
1	Na_3PO_4	0.500	18.00	No good
2	"	0.250	9.00	" "
3	"	0.166	6.00	Fair
4	"	0.083	3.00	Good
5	"	0.041	1.50	"
6	"	0.020	0.76	"
7	"	0.010	0.38	"
8	"	0.005	0.19	"
9	"	0.002	0.09	No good
10	NaOH	1.330	4.80	" "
11	"	0.600	2.40	" "
12	"	0.330	1.20	" "
13	"	0.166	0.60	Quite good
14	"	0.083	0.30	Good
15	"	0.041	0.15	"
16	"	0.020	0.08	"
17	"	0.010	0.04	Fair
18	"	0.005	0.02	Poor
19	"	0.002	0.01	No good

Emulsification occurs with each compound at approximately the same molality. With both of them good emulsification does not occur when solutions more concentrated than .083 (Nos. 4, and 14) are used. Good emulsions are formed within a concentration range of .02–.083 molar. Solutions of NaOH less concentrated than .02 molar (Nos. 17, 18 and 9) are too weak to be of value. But, because of the sodium phosphate's ability to ionize further in extremely dilute solution, this salt will emulsify the oil at concentrations as low as 0.005 molar.

On long standing the emulsions formed by means of the NaOH proved to better withstand the deteriorating action of time. At the end of one month No. 15 was the best of all. It contained 0.041 molar NaOH.

Employing Na_3PO_4 as a detergent for such an oil would entail considerable waste. An examination of the percentage of material needed for emulsification makes this very evident. The emulsification is due, without doubt, to the formation of a sodium soap from interaction of sodium hydroxide and some material in the oil. The oil possessed a decided odor of tar. Some organic derivative was present which formed soap with the alkali.

One mol of Na_3PO_4, in all except very dilute concentrations, yields one mol of NaOH upon ionizing. Outside of this one Na ion the rest of the phosphate is of no value in the process.

For this particular oil, NaOH would serve as a better detergent than sodium phosphate. Much less material would be required and the cleansing should be more perfect.

It is then to be borne in mind, that the ideal compound to be used as a detergent for oils and greases, which contain a material reacting with the detergent, will be determined by the nature of this material. But, as Na_3PO_4 works quite satisfactorily with both, and NaOH works with only one of the oils here studied, it is the safe thing to use the phosphate.

The possibility of a highly "filled" detergent can now be discussed in the light of the facts which have been considered up to this point.

Soap and Silicate Detergent Mixtures

Under the topic of emulsification it has been shown, that the soap concentration of an emulsifying solution should be from 0.05–0.10 per cent at 40° C. Fall[1] has proven that the best soap concentration to employ for the peptization of solids is 0.20–0.40 per cent.

If a particular soap bar were composed of 80% sodium silicate, $(Na_2O)_2(SiO_2)_3$, and 20% soap, and if this detergent were used at a concentration of 0.3%, the actual soap concentration would be $0.3 \times 0.20 = 0.06\%$. This is within the concentration of 0.05 – 0.10 per cent necessary to emulsify oils.

The silicate concentration in the detergent solution would be $0.3 \times 0.80 =$ 0.24 per cent. The MnO_2 value of "S" brand silicate, $(Na_2O)_2(SiO_2)_{3.97}$, at 40° C., is approximately 390.[1] Whereas, the MnO_2 values of the soaps studied, exclusive of olive oil soap, at 0.24% and 40° C. is approximately 520.[1]

This means that the silicate would suspend $390/520 = 75\%$ of the solid material that pure Palm oil, Tallow, Green Arrow, or silicated Green Arrow soap would suspend.

At the above concentration and temperature olive oil soap exhibits an MnO_2 value of about 445.[2] Thus, the silicate would be $390/445 = 87.5\%$ as efficient as pure olive oil soap in the suspension of solids.

By making a bar of soap which contains 20% soap and 80% sodium silicate, the soap would cleanse the liquid dirts, and the silicate would suspend the solids 75–90% as efficiently as would pure soap alone. In reality this percentage would be higher, due to the fact that the soap, as well as the silicate, would suspend the solids to a certain extent.

The emulsifying powers of such a silicated soap were investigated and found to be excellent.

Experimental

A 1.0% detergent solution was prepared containing 0.2% moisture free olive oil soap, and 0.8% moisture free "O" brand silicate $(Na_2O)_2(SiO_2)_{3.05}$.

[1] Fall: J. Phys. Chem., **31**, 801 (1927).
[2] Fall: J. Phys. Chem., **31**, 801 (1927).

This 1.0% solution was diluted to 0.05%, and 25 c.c. of the dilute solution were shaken 20 times at 40° C. with 25 c.c. of kerosene. The emulsions formed were all excellent at the end of 21 hours.

Discussion

Experiments were first made with various percentages of soap and silicate, to make certain that more than 80% silicate would not be efficient. The general conclusions from this work were that 80% silicate was safe to use, and amounts in excess of this, although exhibiting some emulsification, were not to be recommended.

The soap alone does the emulsifying, and in a pure soap solution 0.05 per cent is necessary, but in a solution containing an alkaline substance, such as sodium silicate, which lowers the surface tension, less soap is required.

Consequently, the emulsifying power of a given mix of soap and silicate depends on the concentration at which it is used—for this determines the actual amount of soap present—and on the surface tension lowering caused by the alkali of the silicate.

As can be calculated from the above data, the soap concentration of the 20–80 mixture, used at a concentration of 0.05% is $0.2 \times 0.05 = 0.01\%$. So, due to the alkalinity of the silicate the mixed detergent is quite effective as an emulsifier when the soap concentration is only 0.01%. This, however, would not be a safe concentration to use as it will not always cause emulsification.

From the above discussion, it follows that the 20–80 mix, used at 0.3% and thus possessing an actual soap concentration of 0.06%, possesses a soap concentration which is in excess of that which should be required to cause emulsification in the detergent process.

Although the silicate will not cause emulsification of oils, it will not be inert toward them. For, as has been shown, it possesses detergent ability toward oils by virtue of its "wetting" power.

Seeing that the detergent properties of such a mixture are sufficient to warrant its existence, the question of the mechanical possibility of making such a soap, of the effect of the silicate on the fabric, and numerous other questions immediately arise.

Effect of a Highly Silicated Soap on Factors other than Detergency

The question of the possibility of manufacturing such a soap can be answered only by the factory. They will have to make such a bar and determine if there are any insurmountable difficulties in its preparation. The solubility, and the behavior of such a cake on aging, will be important items.

Carter[1] has shown that the strength of cotton fiber in contact with sodium silicate will increase. This is probably due to a small amount of hydrous SiO_2 adsorbed by the fiber.

Edeler[2] has shown that sodium silicate, because of its ability to form compounds in which the Na_2O:SiO_2 ratio varies, will greatly reduce the free alkali

[1] Carter: Ind. Eng. Chem., **18**, 248 (1926).
[2] Edeler: Ind. Eng. Chem., **17**, 196 (1925).

content of a soap high in this constituent. A soap containing 5.02% free alkali after the addition of sodium silicate, $(Na_2O)_1(SiO_2)_{3.22}$, showed only 0.52% free alkali. This alkali was extracted from the sodium silicate by the alcohol used in the analysis. It was not free, but rather combined alkali. If extraction of the combined alkali from the silicate could be eliminated, the soap would probably show no free alkali.

This property of a silicated soap would be very valuable, for it would keep the free alkali content low. Also, in the manufacturing process the alkali content would not have to be adjusted so carefully, for the silicate would eliminate automatically an excess of alkali left in the soap.

In order to determine the effect that the 20–80 mixture of soap and silicate would have on wool, pieces of red wool were placed in such a solution of 0.3% concentration for a period of 16 hours. The temperature was kept at 40° C. At the end of this time the cloths were rinsed in cold water and were allowed to dry at room temperature. The amount of shrinkage caused by the silicated solution was no greater than that caused by the soap.

Another point worthy of note, was that the dye was much less soluble in the soap-silicate solution than in the pure soap solution.

Microscopical examination of the fibers showed no difference between the cloth treated with the soap and that treated with the mixed detergent.

The water softening properties of this 20–80 mix will be discussed under the next heading. It can be stated here that only toward an iron-hard water will such a detergent possess softening properties equal to soap alone.

One thing decidedly against such a detergent is that it would not possess as strong "wetting" powers as would pure soap.

A detergent of 20% soap and 80% silicate of the correct composition, should offer a detergent to the consumer at a price below that now current, and should at the time increase the profits of the soap manufacturer. These advantages, linked with the fact that the oils used in soap manufacture could be diverted into other channels, should cause such a silicated detergent to enjoy a prosperous market.

Water Softening Properties of a Highly Silicated Detergent

The relative merit of the 20% soap and 80% silicate mixture as compared with pure soap in respect to softening water, was studied.

Experimental

The hard waters used were made by dissolving the correct amount of the various constituents in distilled water to make a 1/1000 molar solution. Such solutions of $MgCl_2$, $MgSO_4$, $CaCl_2$, $CaSO_4$, and $FeCl_3$ were made. Thus, the hardness of these waters was 5.59 grains of $CaCO_3$ per gallon.

A solution of $Ca(HCO_3)_2$ was prepared by passing CO_2 into a suspension of $CaCO_3$ for thirty minutes. The excess $CaCO_3$ was then filtered off. $Fe(HCO_3)_2$ was made by passing CO_2 into a freshly precipitated suspension of $FeCO_3$ for thirty minutes. The undissolved $FeCO_3$ was then filtered off. The strengths of the last two solutions were unknown.

To 10 c.c. of the various hard waters, the detergent solution was added by means of a burette. The containers were oil sample bottles. The end point was taken as the point where sufficient detergent had been added to cause a thin lather to endure for one-half minute after ten successive shakes. The end point was observed with the bottles in a vertical position, and although the standard method is to place the bottles in a horizontal position, the results checked very well and gave an accurate comparison of the amount of detergent required to soften the hard waters. The results are contained in Table XIV.

TABLE XIV

Solution	c.c. Soap Required to soften	c.c. mix Required to soften	Gram ratio of soap-silicate to soap: Difference acc. for	Difference not acc. for
$MgCl_2$	0.95	2.00	2.00	2.158
"	0.95	2.10		
$MgSO_4$	1.00	2.00	1.875	2.025
"	1.00	2.05		
$CaCl_2$	0.90	2.00	4.05	4.22
"	0.95	2.10		
$CaSO_4$	0.70	2.95	4.14	4.37
"	0.65	2.95		
$Ca(HCO_3)_2$	0.35	1.30	3.28	3.71
"	0.35	1.30		
$FeCl_3$	1.10	0.55	0.318	0.5
"	1.10	0.55		
$Fe(HCO_3)_2$	1.15	0.60	0.382	0.51
"	1.20	0.60		

The first of the last two columns (column 4) gives the amount of soap-silicate mixture that is necessary to soften the indicated water as compared to soap alone when .15 c.c. has been subtracted from the soap-silicate readings. This value, .15 c.c., represents the excess of soap-silicate over soap alone, that is necessary to produce a lather in distilled water.

The last column gives the ratio as taken directly from the readings, no correction having been made for the slightly inferior lathering power of the soap-silicate mixture as compared to soap alone.

Discussion

At room temperature the only water softened by the mix as efficiently as by pure soap is the iron-hard water. At first thought, it would appear that the mix was even more efficient than pure soap alone. But if the normalities of the two solutions be figured, it will be seen that the softening of the water is proportional to the normalities of the detergent solutions.

The sodium silicate, $(Na_2O)_2(SiO_2)_{3.05}$, was considered to be two-normal judging the normality on the amount of sodium in the molecule.

The mixed solution = .07406 N

The soap solution = .03670 N

The amount of soap required to soften 10 c.c. iron solution = 1.1 c.c.

Therefore

$$.0368 : .07406 = x : 1.1$$

x = 0.547 c.c. of the mix should have been required
0.550 c.c. of the mix were required.

Effect of adding the Silicate and then the Soap to $FeCl_3$

Experimental

The experiment was conducted as had been the one in which the mixed detergent was added to the solution of $FeCl_3$, except 50 c.c. of $FeCl_3$ were used. Two separate solutions of soap and silicate were made, each solution having the amount of soap or silicate that was contained in the mixed detergent. So, instead of having a solution of 1% detergent, 0.2% of which was soap and 0.8% silicate, two solutions were formed, one of which contained 0.2% soap and the other 0.8% silicate. Thus, 1 c.c. of each solution, a total of 2 c.c., is equivalent to 1 c.c. of the mixed detergent.

2.8 c.c. of the mix is required to soften 50 c.c. of 1/1000 M $FeCl_3$, Table XV gives the amount of the separate detergents necessary.

TABLE XV

Amount separate detergents necessary to soften 50 c.c. 1/1000 M$FeCl_3$ at room temperature

c.c. 0.8% Silicate	c.c. 0.2% Soap	Extent of Foam
2.25	2.25	None
2.35	2.35	Very small
2.40	2.40	Good. Practically the same as when 2.8 c.c. of the mixed solutions are used.
8.40	8.40	necessary to fill vessel with foam.

8.25 of mix necessary to fill vessel with foam.

Discussion

The above data show that the advantage gained by adding the silicate to a water containing $FeCl_3$ before the soap is added, is very small.

Effect of High Temperature on Water Softening Ability of Mix

Richardson[1] has done some work on the softening of water by soap-silicate mixtures. His investigations include some experiments at high temperatures.

The results obtained by Richardson at room temperature agree with those found in the present work, namely, that the silicate has very little effect on

[1] Richardson: J. Ind. Eng. Chem., **15**, 241 (1923).

the water containing calcium salts, but does have an apparent effect on water containing magnesium salts.

At 100° C. the effect on the calcium salts is only very slightly increased, while the effect on the magnesium salts is vastly increased. In fact, at this temperature the silicate softens the water equally as well as does an equivalent amount of soap.

Richardson states that at 100° C. the silicate in some instances possesses more soap saving powers than would be expected. In all of these experiments, save one, the soap silicate solutions possessed an increased ability, above that of soap alone, to soften the $MgCl_2$ solution, only in so far as the normality of the soap-silicate mixture was larger than that of the pure soap solution.

In one instance, 12.5 c.c. of a 0.0328 normal soap solution were required to soften a definite amount of water, whereas, 6.00 c.c. of a 0.0414 normal soap-silicate solution were sufficient.

$$.0328 : .0414 = x : 12.5$$

$x = 9.9$ c.c. of the mix should have been required if the mix reacted with the $MgCl_2$ in the same manner as the soap alone. 6.00 were all that were actually needed.

Outside of this one instance, the soap and soap-silicate mixtures behaved identically, when their normalities were considered. It would hardly seem just to conclude from this one case that sodium silicate has any unexpected or unexplainable soap-sparing properties when used with waters containing $MgCl_2$.

Difficulty was experienced in duplicating the work of Richardson which showed that silicate was of as much value as soap in softening $MgCl_2$ hard water at 100° C. This was due to the fact that at the concentration Richardson used, 0.0025 molar $MgCl_2$, and at a temperature of 100° C., the olive oil soap used in the present work reacts with the $MgCl_2$ much slower than the sodium oleate Richardson used. Because of this, a foam is produced with the olive oil soap before the water is actually softened.

As a general conclusion, it can be stated that at room temperature sodium silicate mixed with soap is of extreme value as a softener of water containing iron, of considerable value as a softener of water containing magnesium, and of very little worth as a softener of water containing calcium. At 100° C., its value as a softener of magnesium hard water is greatly enhanced, while the increase in temperature increases the silicate's effectiveness on waters containing calcium to only a very limited extent.

Iron Stain

There was a possibility that the detergent composed of 20 parts of soap and 80 parts of silicate might have more ability in preventing, or removing iron stain from fabrics than would pure soap. Experimentation on this point proved conclusively that the mix behaved toward iron stain exactly as would a pure soap solution.

Ability of NaOH and Na_2CO_3 to soften Water containing Iron

Sodium silicate is an alkaline salt and, as the above work has shown, is very effective in softening water containing iron, either when it is mixed with soap or is added to the iron solution alone. The effectiveness of the alkalis, NaOH and Na_2CO_3, as compared to sodium silicate was investigated.

Experimental

50 c.c. and 10 c.c. portions of 1/1000 molar $FeCl_3$ were used. The NaOH had a normality of 0.1057, and the Na_2CO_3, 0.1078.

0.2 c.c. of 1% olive oil soap solution were necessary to give a good lather with 50 c.c. of distilled water, on shaking ten times. Thus, after each addition of NaOH, or Na_2CO_3, 0.2 c.c. of the soap solution were added and the bottle shaken ten times, Table XVI.

TABLE XVI

c.c. $FeCl_3$	c.c. NaOH	Foam	c.c. Na_2CO_3	Foam
50.0	1.3	No	2.3	No
"	1.4	"	2.4	"
"	1.5	Yes	2.5	Meagre
"	1.5	"	2.8–3.0	Yes
"	1.6	"		
10.0	0.2	No	0.4	No
"	0.3	Slight	0.5	"
"	0.35	Yes	0.6	Yes

The Na_2CO_3 was also investigated at 40° C. and 100° C. with no apparent change in the necessary value to effect softening.

Discussion

The NaOH is much superior to Na_2CO_3 for softening water containing iron. The solutions containing 3.0 c.c. of Na_2CO_3 are inferior in their lathering properties to those containing only 1.5 c.c. of NaOH. The NaOH seems to effect softening at a definite point, whereas, the Na_2CO_3-softened solutions start to lather slightly after 2.5 c.c. have been added, and after 2.8–3.00 c.c. have been added they show lather of sufficient quantity to call this the end point.

When the amount of NaOH necessary to cause softening has been added to the solution, the iron does not precipitate but stays in a colloidal state. Cataphoresis experiments upon such a solution showed the solution to be negatively charged. An excess of NaOH will flocculate this colloid, and a short period of standing in an open vessel will do likewise. It is more permanent in a closed container. This is probably due to the carbon dioxide in the air.

The Na_2CO_3-softened solutions do not exhibit this tendency to stay in the colloidal state, until from 3.5 to 3.7. c.c. of the Na_2CO_3 have been added to 50 c.c. of the $FeCl_3$ solution. Then the permanency of the sol is only about five minutes, and it flocculates immediately if soap is added. When 4.0 to 4.5 c.c. of $NaCO_3$ have been added, the solution does not flocculate com-

pletely with the addition of soap; but precipitation is complete after standing overnight. While solutions containing 1.6 c.c. of NaOH in a closed bottle do not flocculate overnight.

These facts have been quoted in an effort to account for the superiority of NaOH over Na_2CO_3 as a softener of water containing iron. It seems to be due to the greater ability of the NaOH to form a negative sol from the positive iron colloid.

Soap itself is in all probability a negative colloid, and thus precipitation does not occur when it is added to a sol which is negative. This would look as though at least part of the precipitation of soap by an iron solution were due to mutual flocculation of the two sols, and not simply to a reaction forming an insoluble iron soap.

Iron solutions softened with sodium silicate tend to stay colloidal, as was the case with NaOH. These solutions on cataphoresis are likewise proved to be negative sols.

NaOH is 139.2%, and Na_2CO_3 73.2%, as efficient as sodium silicate in softening water containing iron. But the sodium silicate would be superior to either NaOH or $NaCO_3$ if the compounds were to be incorporated into a bar of soap, for NaOH would tend to change to Na_2CO_3 in the air.

The superior ability of sodium silicate and sodium hydroxide, as compared to sodium carbonate, in softening water containing iron may be attributed to the ability of the first two compounds of forming a negative sol of the iron solution. Thus, the amount of the substances necessary to cause softening would depend on the amount of adsorption and not on the amount necessary to precipitate the iron solution.

The absence of precipitation probably also keeps much soap from being occluded, and thus carried away with the precipitate.

During the process of studying sodium silicate the following topic was investigated as an interesting digression:

The Effect of Sodium Silicate on NaClO Bleach

Carter[1] has shown that sodium silicate added to a bleaching solution of sodium hypochlorite conserves the strength of the bleaching solution when it is in contact with a bleachable material, increases the strength of the fabric for the first fifteen minutes that it is in contact with the hypochlorite, and after this time causes the loss in strength to be less than if no silicate were present, and improves the color of the article being bleached.

The first two phenomena are easily explained. But Carter seems to have overlooked, or else was not interested in the reason for the facts noted by him.

Sodium silicate is a basic salt. NaClO bleaches according to the following:

1. $NaClO + HOH \rightleftarrows NaOH + HClO$
2. $HClO \rightleftarrows HCl + (O)$

The formation of the instable HClO, which yields the nascent oxygen for the bleaching, is directly proportional to the hydrogen ion content of the solution. The activity of the solution would be greatly increased by the addition

[1] Carter: Ind. Eng. Chem., **18**, 248 (1926).

of an acid. The reverse is likewise true, and the addition of a substance such as sodium silicate, which will reduce the hydrogen ion content, will decrease the activity of the bleaching solution. This means that any bleachable material present will be attacked by the hypochlorite solution less rapidly than though no silicate were in the solution. Such a state of affairs would be analogous to using a less concentrated bleach. For this reason the available chlorine was conserved simply because it was not free to act.

The above theory was easily demonstrated by passing blue-colored cloths through three solutions of the same bleach, one solution containing some silicate, and one of the other two an equivalent amount of NaOH. The cloth treated in the solution containing the NaOH lost the least color, the one in the silicate lost more, and the one in the bleaching solution containing no alkali lost practically all of its blue color. This means that, in a given period of time, the solution containing no alkali had done more bleaching than those that contained a larger concentration of hydroxyl ions. Because the solution containing the hydroxide contained more hydroxyl ions, it was less active than the one containing the silicate. So the cause of the chlorine conservation in a bleaching solution, when silicate is present, is readily understandable.

The explanation of the fiber-strengthening caused by the addition of silicate to a bleaching solution is practically the same. NaClO solutions weaken the fabric fibers, and the extent of this weakening is directly proportional to the strength of the bleaching solution. Carter treated two fabrics with identical bleaching solutions, with the exception that one solution contained some sodium silicate. He found that during the first fifteen minutes the tensile strength of the cloth immersed in the bleaching solution containing the silicate actually increased, and after this time the loss of strength was less than that shown by the cloth in the solution containing no silicate.

The rise in the tensile strength can be explained by the fact that silicon dioxide is adsorbed by the fibers, and the increased strength caused by this adsorption is greater during the first few minutes than the decrease in strength caused by the bleaching solution. The adsorption of SiO_2, probably in hydrous form, is proven by Carter, for he found the ash content of the fabric to increase with exposure to silicate solutions. The fact that the loss in fabric strength is less with the silicated bleaching solution, is plainly understood from the foregoing explanation of the effect that an alkali has on a bleaching solution. Due to the increased hydroxyl ion concentration caused by the addition of the silicate, the bleaching solution is not as active as though the silicate had not been added. The loss in strength by the fibers is proportional to the strength of the bleaching solution. The solution containing the silicate was less active, which amounts to the same as though it were less concentrated, and therefore the cloth in this solution was not bleached as severely as the one in the solution containing no silicate. Consequently, less decrease in fiber strength would occur.

The explanation of why the silicated bleaching solution imparted a better color to the fabric, was not so easily determined. Bancroft[1] has shown that

[1] Bancroft: J. Phys. Chem., **19**, 159 (1915).

oxycellulose is soluble in dilute alkalies. It was possible that the whiter color, obtained by bleaching with a solution containing silicate, might be due to the solvent action of the alkaline silicate upon a small amount of yellow oxycellulose formed during the bleaching. However, extensive experimentation on this point did not bear out the theory.

Experimental

A sodium hypochlorite solution was made by electrolyzing 500 c.c. of a 5 normal solution of NaCl, containing 0.25% of $Na_2Cr_2O_7$, between carbon electrodes with 10 volts and 5 amperes for forty-five minutes, at a temperature of 10°–15° C.

Colored, and unbleached cotton were treated with the above solution when it contained 1% NaOH, 1% $(Na_2O)_2SiO_2)2.05$, 0.5% NaOH, 0.5% $(Na_2O)_1$ $(SiO_2)2.05$ and when no addition agent had been added. Of course, the rapidity and extent of the bleaching was less with the silicated solutions, and least with the solutions containing the hydroxide. But in no case was a whiter product obtained by the use of the alkaline salts.

No evidence of the formation of oxycellulose was obtained, nor was a more perfectly bleached product secured by the addition of sodium silicate to the bleaching solution.

The above experiments were repeated at 50° C. and the same results were obtained. A weaker solution, made by diluting the original to one-fifth of its former strength, was used at 50° C. with no change in results.

Gaseous chlorine was used as the bleaching agent. In no case was there any evidence of the formation of yellow oxycellulose.

In summary it can be stated that, during the bleaching process, the formation of oxycellulose was not apparent, and that the bleaching solution containing sodium silicate differed in its effect from that containing no silicate, only in acting more slowly.

During the above experimentation, it was noticed that occasionally the cloth that had been dipped in the silicated bleaching solution was whiter than the one treated to a pure bleaching solution. This usually happened when the fabric was washed very superficially after the NaClO treatment. Further experimentation proved this to be the case. A white cheesecloth was treated to the bleaching solution, made by the electrolysis of salt as previously described. A second cloth was treated to the same solution, which contained 0.5% $(Na_2O)_1$ $(SiO_2)2.05$, Table XVII.

TABLE XVII

White cloth in.	Washing treatment	Color
Pure bleach	Passed once under cold water tap	Slightly yellow
Silicated bleach	" "	Practically white

These samples were dried at room temperature. The yellow color of the cloth treated with the pure bleach was practically all removed by washing with soap.

A bleaching solution was prepared by passing chlorine into an iced 10% NaOH solution. NaOH was then added until the reaction was slightly basic. This was diluted to one third its former strength. One solution of the pure bleach and one containing 0.5% $(Na_2O)_2$ $(SiO_2)2.05$ were used. The white cheesecloths were placed in one or the other solution for thirty minutes, at a temperature of 50° C. They were then washed once in cold water, were wrung out, and were dried in an oven at 110° C.

The cloth which had been treated with the pure bleach had become slightly yellow, whereas, the one treated with the silicated NaClO was much whiter. When the cloth, which had turned yellow, was washed thoroughly with soap, it became whiter, but not as white as the original.

When the cloths were dried at room temperature, the yellow color of the cloth treated with the pure bleach could be washed out practically entirely.

When the fabrics were washed thoroughly before drying, no difference in the color caused by pure bleach and silicated bleach was noted, nor was any yellow color imparted to a cloth which had been white before the treatment.

Discussion

The experiments quoted above prove that sodium silicate in a bleaching solution of sodium hypochlorite facillitates the easy elimination from the fabric of some yellow product formed during the bleaching process.

The cloths used in this work were very small, usually not over two or three inches square. Thus, if differences in color caused by incomplete washing were apparent with such small cloths, it is more than likely that such was also true in Carter's work, for he used cloths of much larger size, which could not be washed as easily.

It will be noted that, when the fabric was dried at room temperature after the bleaching treatment, the yellow tinge could be nearly eliminated by washing with a soap solution. However, if the material were dried at a temperature of 100° C., or over, the yellow color was "set" and could not be removed by soap and water. Carter ironed his fabrics after the bleaching treatment, and in this way made the color permanent. This treatment with heat also tends to increase the intensity of the color.

The reason that the cloths treated with silicated bleach did not show the intense yellow color of those not so treated, may be attributed to SiO_2 adsorbed by the fiber. Such adsorption would tend to prevent the adsorption, or absorption, of any yellow decomposition product by the fiber, and, if oxycellulose were formed, would tend to keep this at a minimum.

That SiO_2, probably in a hydrous form, is adsorbed on the fiber is established by Carter's work. Such a process was likewise indicated in this investigation, for the fabrics immersed in silicated bleaching solutions always had a more stiff and less flexible "feel" than those not so treated.

The better color, obtained when cotton is bleached by sodium hypochlorite solutions if a small amount of sodium silicate is added, may be attributed to the greater ease with which a cloth so treated can be freed from

contaminating substances formed by the bleaching process. This is unquestionably an advantage, and is sufficient reason for adding silicate to bleaching solutions. However, extensive washing with soap and water after the bleaching treatment, before the fabric is allowed to dry, should have the same effect.

Summary

The general results of this investigation are as follows:

1. Soap solutions will suspend solid material stably because the solid particles become charged by adsorption of negative ions from the solution. The existence of an optimum value of soap concentration for this stabilization is due to the fact that the positive ions are also adsorbed from the solution. The soap concentration in which the ions are adsorbed to the same extent will cause no stabilization, and the concentration in which there is strong adsorption of the positive ion will give the optimum stabilization.

2. The amount of solid material carried through filter paper by soap solutions should parallel the amount stably suspended. Therefore, McBain's and Fall's results should agree. They are found to do so when the carbon suspensions, used by McBain, are so treated that the non-stabilized carbon does not retard the passage of the stabilized material through the filter paper.

3. The optimum concentration of soap for the suspension of solids, 0.2-0.4%, is more than sufficient for the emulsification of oils, this requiring 0.05–0.10%.

4. A concentration of soap above that necessary to cause emulsification is not harmful, but is beneficial to emulsification.

5. Palm Oil, Olive Oil, Tallow, Commercial Green Arrow, and Commercial Silicated Green Arrow Soaps vary only to a limited extent in their emulsifying powers.

6. High temperatures are detrimental to emulsification, as well as to suspension. A temperature of 40° C., (104° F.,) is recommended.

7. Alkaline salts aid emulsification. NH_4OH, Na_3PO_4, and NaOH are very efficient. Beneficial results are obtained when the emulsifying solution contains 1.2 per cent NH_4OH, or .32% NaOH. NH_4OH is not detrimental when present in excess, whereas NaOH and its salts are.

8. Sodium silicate is not an emulsifying agent.

9. The importance of wetting as a factor in detergency has been studied. The reason for highly concentrated soap solutions possessing good detergent value is because such solutions are extremely efficient wetting and emulsifying agents.

10. The reason that sodium phosphate is of such value as a detergent for greases containing calcium oleate is due to its ability to form sodium soap from the calcium oleate present. This process disintegrates the grease; causes the sodium soap to become thoroughly incorporated in the grease; and removes the calcium oleate, which substance emulsifies water in oil and works in opposition to the soap. The wetting ability of the sodium phosphate is also a factor.

11. One specific transmission grease, manufactured by the Deyo Oil Co., was emulsified more efficiently per gram of detergent, by NaOH than by Na_3PO_4. Cleansing would occur in the same order. The grease presumably contained some organic material, which formed soap with the compound added.

12. The possibilities of a detergent compound of 20% soap, and 80% sodium silicate of the correct composition, have been shown to be worth considering. The effect of such a detergent upon water softening, content of free alkali, and upon the textile fibers has been discussed.

13. Sodium hydroxide is more efficient than sodium silicate, and sodium carbonate less so, in softening waters containing iron.

14. The reasons for the beneficial effects obtained by adding sodium silicate to a bleaching solution are as follows:

First, the loss in strength of the solution is retarded, because the alkaline nature of the silicate forces back the reaction forming HClO. This compound is unstable and decomposes, and thereby weakens the bleaching solution.

Secondly, the cloth fibers are only slightly weakened because they are bleached less than if no silicate were present. The loss in fiber strength is proportional to the amount of bleaching, this is in turn proportional to the amount of HClO present, and, as stated above, the sodium silicate retards the formation of this substance. Also some SiO_2 is probably adsorbed which strengthens the fibers.

Thirdly, in the bleaching process some slightly yellow decomposition product is formed, which is rather difficult to wash out of the cloth. The presence of sodium silicate in the bleach facillitates the removal of this substance.

Acknowledgments

To acquire a sense of values, to be able to assign to each factor of existence its proper weight, is one of life's most difficult tasks. To be commended and emulated is the man who possesses this ability. Fortunate is the individual who comes under his direction. This privilege was accorded the writer by executing the work herein reported under the personal direction of Professor W. D. Bancroft. For his beautifully sane view of life, for his inspiring personality, and for his ever ready willingness to help, the writer wishes to acknowledge his gratitude.

As the recipient of the generous Palmolive Fellowship for two years, the writer is most grateful to the Palmolive Company of Milwaukee, Wisconsin and to the awarding committee.

The kind assistance of the Premier Mill Corporation of Geneva, New York, which disintegrated some of the carbon used in these experiments, is greatly appreciated.

Cornell University.

SOME OBSERVATIONS ON THE SYSTEM PHENOL-WATER

BY EDWARD RICHARD JONES

Whilst investigating the depression of the freezing point of water by phenol, two eutectic points were observed, solid phenol-solution-ice and phenol hydrate-solution-ice. The existence of a hydrate of phenol was first described by Calvert[1] who obtained it by cooling a mixture of four parts of phenol and one part of water to 4° C.; and Smits and Maarse[2] definitely showed it to have the formula $(C_6H_5OH)_2.H_2O$. But this compound, it appears, is very difficult to prepare. Paternò and Ampola[3] in their determination of the melting point line of phenol in the system phenol-water, overlooked it, because the formation of the hydrate very often does not take place, and Alexejeff[4] being unable to obtain evidence of a definite compound, concluded that the hydrate described by previous workers was merely a mixture of phenol and water. Smits and Maarse, as well as Rhodes and Markley,[5] were unable to obtain it by the original method of preparation. They state that a solution of 15% of water in phenol must be cooled for an hour at −78°C. before crystals of the hydrate can be obtained, but during the present work, the hydrate occurred spontaneously when the temperature of the solution was not lower than −1°C., which rather supports the view of Calvert and of Lowe and Gill[6] that very low temperatures are not essential for its preparation. Having once prepared a small amount, quantities required for further work were easily obtained by cooling concentrated solutions of phenol below 12°C., and "seeding" with a crystal of the hydrate.

A review of the literature shows that the system phenol-water has been studied by several investigators, but that portion of it below 13°C., not very fully by any of them: more attention has been paid to that part dealing with the concentrations of the phenol and water in the two layers at different temperatures. The temperature given in the literature for the eutectic point, phenol hydrate-solution-ice, varies from −0.85° to −1°C; that of the invariant point, solid phenol—phenol-rich solution—water-rich solution, from 1.5° to 1.7°C. Further, there appears to be no reference to the invariant point, phenol-rich solution—water-rich solution—ice, and figures for the solubility of phenol hydrate are not available.

In view of the rather meagre and contradictory nature of previously published information, and as the hydrate could be easily obtained, it was considered advisable to study a portion of the system more carefully, and to

[1] J. Chem. Soc., **18**, 66 (1865).
[2] Ver. Kon. Akad. Wet. Amsterdam, **20**, 100 (1911-12).
[3] Gazz., **27**, 523 (1897).
[4] J. Soc. Chem. Ind., **1**, 397 (1882).
[5] J. Phys. Chem., **25**, 527 (1921).
[6] Chem. News, **31**, 32 (1875).

attempt to obtain the temperature of the invariant point, phenol-rich solution—water-rich solution—ice. This paper, then, deals with investigations carried out at temperatures below 13°C., and under atmospheric pressure, which has been assumed constant throughout.

Experimental

The phenol used in all the experiments was purified by being fractionally crystallised three times and distilled twice, the second distillation being carried out over anhydrous copper sulphate, and the portion boiling at constant temperature only collected. The final product was pure white, and not hygroscopic. As a criterion of purity, a determination of the freezing point was made. The phenol was distilled directly into the freezing point tube, the necessary precautions to prevent the access of air being taken, and remelted. The tube, containing stirrer, thermometer (calibrated to 0.01°C.), and a tube by means of which a current of dry air could be passed through the apparatus, was then placed in an air jacket in a bath at a temperature not more than 0.5°C. below the true freezing point. The liquid was gently stirred, and temperature readings taken every half minute: a rapid current of dry air was passed through the tube the whole time the phenol was exposed to the air. Several determinations were made, using different samples of phenol. In every case, there was a slight supercooling of about 0.1°C., after which the temperature rose and remained constant for several minutes. The freezing point was also determined in the presence of anhydrous copper sulphate, but no difference was observed. The values obtained were between 40.69° and 40.72°C., and the mean, 40.71°C. is considered to be the true freezing point of phenol. The recorded values for the freezing point vary considerably: Béhal and Choay[1] give a value as high as 42.5°-43°C. Lowe[2] gives the value as 42.25°C. But it is worthy of note that all later workers who have taken special precautions to obtain a pure sample of phenol, favour the lower value, e.g. Hulett,[3] 40.8°C; Tammann,[4] 40.6°C; Rhodes and Markley, 40.8°C.

The concentrations of phenol in solutions in equilibrium with phenol-rich solution at 13°C., with the hydrate and with phenol-rich solution at 9.93° and 4.93°C., as well as those in solutions in equilibrium with the hydrate, phenol-rich solution, and solid phenol at 0°C., have been determined by solubility measurements. Previous investigators have almost invariably used the synthetic method: solutions of known strength were made up and their freezing points determined. But it was considered that solubility measurements would give more reliable information. The solutions, together with excess of hydrate, solid phenol, or phenol-rich solution, as the case might be, were placed in glass-stoppered bottles which were practically immersed in a thermostat kept at the required temperature,—the thermostat wash and regulated to 0.05°C. Vigorous shaking of the bottles to hasten equilibrium

[1] Compt. rend., **118**, 1211 (1894).
[2] Chem. News, **16**, 57 (1867).
[3] Z. physik. Chem., **28**, 663 (1899).
[4] "Kristallisieren und Schmelzen," 308 (1903).

was not possible with solutions containing excess phenol-rich solution, as the emulsion formed by shaking does not readily settle. Hence, these solutions had to be carefully and gently stirred: the time of attaining equilibrium was thus considerably longer, from six to eight hours being required.

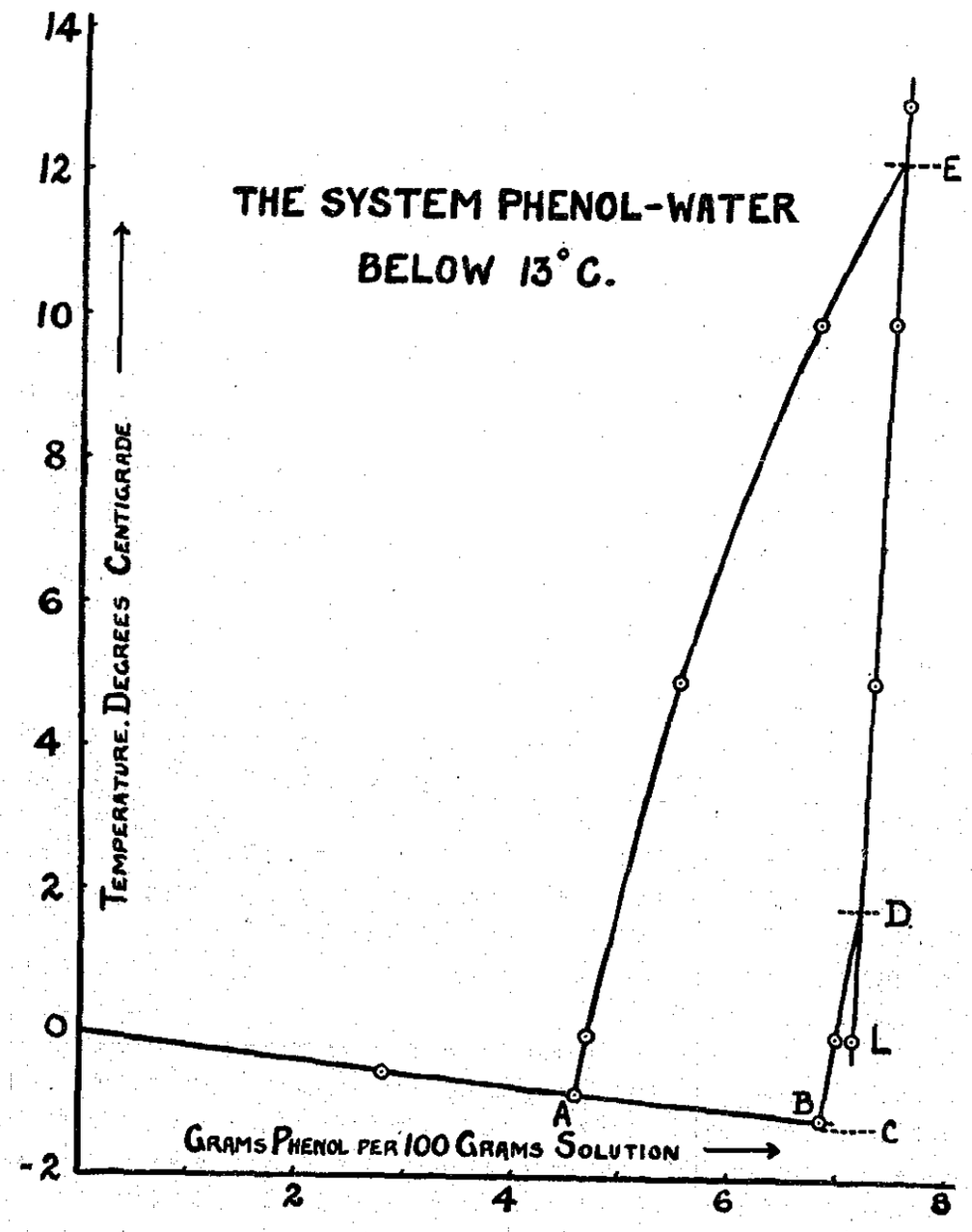


FIG. 1

The phenol solutions were analysed by the method given by Redman, Weith and Brock.[1] It was found, however, that analyses of the necessary accuracy were obtained only when the phenol solutions used were less than N/20, i.e. half the strength recommended by these authors,—solutions of this strength require approximately 40 ccs. of N/10 KBr, $KBrO_3$ solution. All the phenol solutions obtained during this work were stronger than N/20,

[1] J. Ind. Eng. Chem., 6, 389 (1913).

and so weighed quantities were taken and diluted to a known volume so that the resulting solution was as nearly as possible N/20. Duplicate analyses were done in every case, and these usually agreed to within 0.1%. The solubility measurements were repeated until constant values were obtained.

The results obtained are given in Table I. and illustrated graphically in Fig. 1. AE is the solubility curve of the hydrate, which is the stable form

TABLE I

	Grams phenol per 100 grams solution in equilibrium with		
Temp. °C.	Phenol-rich Soln.	Phenol Hydrate	Solid Phenol
13.0	7.574		
9.93	7.454	6.771	
4.93	7.308	5.530	
0.	7.147	4.695	7.005

below 12°C. LE, meeting the curve AE at E, the invariant point, phenol hydrate—phenol-rich solution—water-rich solution, is the curve of equilibrium between phenol-rich solution and water-rich solution, and BD represents the solubility of the solid phenol. The liquid phase rich in phenol, and solid phenol, being unstable below E, their solubilities are greater than that of the hydrate.

The melting points, under water, of the hydrate and of phenol have been determined, and are given in Table II. These temperatures are represented

TABLE II

Substance	Phenol	Phenol Hydrate (under water)	Phenol (under water)
Melting Pt. °C.	40.71	12.17	1.80

by the dotted lines in the diagram, cutting the solubility curves at D and E. D is another invariant point, solid phenol—phenol-rich solution—water-rich solution. A thick paste of the hydrate and water was placed in a large test tube fitted with a thermometer and a stirrer. This was warmed up to a temperature of about 16°C., the liquid being stirred to remove all traces of the hydrate, and afterwards cooled to 11.5°-12°C. The test tube was then quickly placed in an air jacket contained in a bath, the temperature of which was kept about 0.2° lower than the melting point, and a small quantity of the hydrate added. The temperature rose fairly quickly, and the highest point reached was taken as the melting point of the hydrate. The mean of several readings has been taken. The same procedure was adopted for the melting point of the phenol (under water), but at the lower temperature, and the seeding being done with solid phenol. The values obtained for these two points agree very closely with those of previous workers.

The observations on the lowering of the freezing point of water were carried out by the equilibrium method previously described,[1] and are represented by the curve OAB in the diagram. The eutectic points A and B, phenol hydrate, solution, and ice, and solid phenol, solution, and ice respectively, were obtained in the usual manner, but the temperature at the invariant point, phenol-rich solution—water-rich solution—ice, represented by the dotted line at C in the diagram, was obtained indirectly. A quantity of finely crushed ice was added to the freezing point flask, into which a saturated solution of phenol, together with an amount of free phenol-rich solution sufficient to be in excess at the equilibrium temperature, had already been placed. The whole apparatus was assembled, and allowed to cool in the bath to a temperature of about -1.2°C., before stirring was attempted. The mixture was then well stirred to ensure thorough mixing, and the temperature, which remained constant for a considerable time, noted. On continuing the stirring, the temperature suddenly rose to that of the eutectic point, solid phenol-solution-ice. This temperature was again noted, and as a further check, the temperature of the hydrate eutectic point determined by inoculating the solution with a little of the hydrate. By difference, it was found that phenol-rich solution, water-rich solution, and ice coexist in metastable equilibrium at -1.252°C. The whole procedure was repeated, and the determinations agreed within the limits of experimental error. A direct determination of the concentration of the phenol at this point was not possible, because the emulsion formed did not settle. By extrapolation from the graph, the concentration at C would be 7.14 grams phenol per 100 grams solution, and the temperature -1.20°C., a value somewhat different from that actually observed. There appear to be three possible explanations to account for this difference. Firstly, the solubility of the unstable phenol may increase below 0°C., cf. nicotine and water.[2] Secondly, phenol-rich solution is present as an emulsion, which may be appreciably more soluble than phenol-rich solution in mass: this is scarcely probable, as the temperature is reproducible. Thirdly, there may be a change in the direction of the depression-concentration curve between B and C. Along OB, the concentration increases more rapidly than the depression, and the curve is slightly convex to the axis of concentration, but between B and C, the depression-concentration curve may become concave to this axis. This anomalous behaviour has also been observed with concentrated solutions of butyric acid, which is reported to separate into two layers.

TABLE III

Temperature °C.	−0.534	−0.843*	−1.174*	−1.252
Grams Phenol/100 gms. soln.	2.803	4.607	6.839	

*Eutectic temperatures.

[1] Phil. Mag., (7) 3, 1032 (1927).
[2] Hudson: Z. physik. Chem., 47, 113 (1904).

The results of the freezing point determinations are given in Table III; where the eutectic temperatures are marked with an asterisk.

It will be observed that in this portion of the phenol-water system, there are two eutectic points, A and B, and five invariant points, A, B, C, D, and E; and the region BDLC is doubly unstable,—unstable with respect to the metastable curve BD, and the stable solubility curve AE.

Summary

The system phenol-water has been studied below 13°C. Two eutectic points, and the temperature at the doubly unstable invariant point, Phenol-rich solution—water-rich solution—ice, have been observed. Solubility measurements have also been made. The freezing point of pure phenol is given at 40.71°C.

I am indebted to the University of Wales for a Postgraduate Studentship during the session 1926-27, and to Mr. C. R. Bury for his valuable advice during the course of this work.

Edward Davies Chemical Laboratories,
University College of Wales,
Aberystwyth.
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IONIZATION PRODUCED BY RADON IN SPHERICAL VESSELS

BY GEORGE GLOCKLER

In the study of the chemical effects of alpha particles produced by gaseous radon and its decomposition products Ra A and Ra C, it has been customary to calculate the ionization by means of the average path law, as developed by Lind[1] and Lunn[2]. However, Mund[3] has lately deduced expressions for the total ionization by considering the losses of ionization caused by the fact that some of the alpha particles are intercepted by the wall of the reaction vessel before they have completed their range. Mund makes two assumptions in his derivation: first he assumes the validity of Geiger's law and second, that all of the Ra A and Ra C reach the wall before they decompose.

In this paper we shall develop the average path law in such a form that it can be compared with the equations of Mund. We shall also indicate a new derivation of his equations, but in our method we shall follow closely the geometrical picture used in the derivation of the average path law. Finally we shall present arguments for a correction to be applied to Mund's equations. The correction has to do with the assumption stated above that all of the Ra A and Ra C decompose on the w ll. It will be shown that experimental data exist which indicate that only about 70% of Ra A and nearly all of Ra C (93%) decompose on the wall.

The following notation is used:

N_o = number of Rn atoms present initially
t = time
r = range of α pt. from Rn = 3.94 cm; (air N.T.P.)
r' = do. from Ra A = 4.50 cm.; $r' = ar$; $a = 1.142$
r'' = do. from Ra C = 6.57 cm.; $r'' = br$; $b = 1.667$
$I_1 = Kr^{2/3} - K(r - x)^{2/3}$ = ionization produced by an α pt. from Rn in the distance x (Geiger's Law).
I_2, I_3 = do for Ra A and Ra C.
$K = 6.74 \times 10^4$ at N.T.P.
λ = decay constant for Rn.
R = radius of the spherical reaction vessel
$\rho = \frac{r}{R}$
$B = N_o(1 - e^{-\lambda t})\,Kr^{2/3}$; $N = N_o(1 - e^{-\lambda t})dV/V$
$\bar{p}$ = average path of an α particle
$\bar{p} = \frac{3}{4}R$ for Rn and $\frac{1}{2}R$ for Ra A and C on the wall.
I_x = Intensity of Ionization (Ionization per cm. path)
V = Volume of reaction vessel
n = fraction of Ra A decomposing in gas phase
m = do of Ra C

[1] J. Phys. Chem., **16**, 564-613 (1912).
[2] Lind: "Chemical Effect of Alpha Particles and Electrons," **82** (1921).
[3] Ann. Soc. Scient. Bruxelles, **44**, 336 (1925); J. Phys. Chem., **30**, 890 (1926).

I. The Average Path of Alpha Particles in a Spherical Vessel filled with Radon

Consider in Fig. 1 N radon atoms decomposing in time t at the point P. Then the number of alpha particles leaving P in all directions (all directions are equally likely) in time t will be the same. The number dN that will leave in direction θ and describe paths of length x is given by

$$\frac{N}{4\pi x^2} = \frac{dN}{2\pi x^2 \sin\theta \, d\theta} \tag{1}$$

The total path that all the alpha particles will describe which leave P will be

$$\int_o^\pi x \, dN = \frac{N}{2} \int_o^\pi x \sin\theta \, d\theta$$

and the average path will be

$$\bar{p} = \frac{\frac{N}{2} \int_o^\pi x \sin\theta \, d\theta}{N} \tag{2}$$

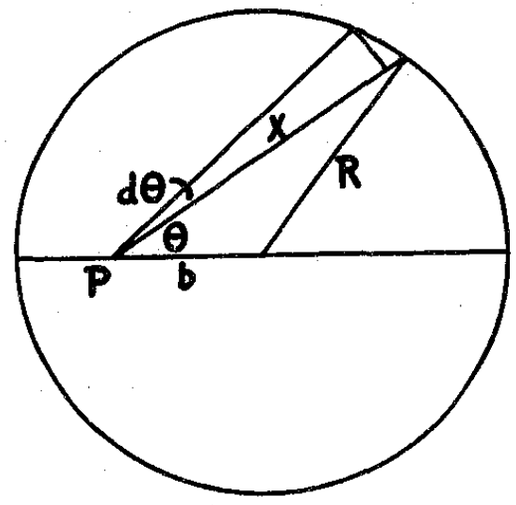


FIG. 1

By the help of the cosine law x can be expressed in terms of θ and the integration yields the result obtained by Lunn.[1] A further integration over the whole spherical volume gives the average path

$$\bar{p} = .75 \, R \tag{3}$$

If it is assumed that all the Ra A and Ra C decompose on the wall, then the average path of the resulting alpha particles is given by the same method

$$p = .5 \, R \tag{4}$$

and for all three sets of alpha particles combined

$$\bar{p} = .5833 \, R \tag{5}$$

We have here sketched the method of deriving the expression for the average path so that it can be compared with the method of deriving Mund's equations in Section IV. It will then be seen that the simple proportion indicated in equation I is the fundamental thought underlying both methods of treating the problem of calculating the ionization produced in spherical vessels.

II. The Average Path Law (Theoretical Expression)

We may now write the average path law as follows:

The ionization of $N_o(1 - e^{-\lambda t})$ alpha particles from radon in time t is

$$I_1 = N_o(1 - e^{-\lambda t}) \, Kr^{3/5} \left[1 - \left(1 - \frac{\bar{p}}{r} \right)^{3/5} \right] \tag{6}$$

if we assume Geiger's law and since the average alpha particle will of course traverse the average path. Similar expressions are obtained for the ionization due to

[1] Lind: "Chemical Effect of Alpha Particles and Electrons," 83 (1921).

the alpha particles from Ra A and Ra C if we assume that they reach the wall before decomposing.

The total ionization due to all three sets of alpha particles in time t is given by

$$I = B\left[1 + a^{2/3} + b^{2/3} - \left\{\left(1 - \frac{3}{4\rho}\right)^{2/3} + \left(a - \frac{1}{2\rho}\right)^{2/3} + \left(b - \frac{1}{2\rho}\right)^{2/3}\right\}\right] \quad (7)$$

For large values of ρ this expression may be expanded binomially:

$$I = \frac{B}{\rho}\left[\frac{1}{2} + \frac{1}{3\sqrt[3]{a}} + \frac{1}{3\sqrt[3]{b}}\right] = B\,\frac{1.10}{\rho} \quad (8)$$

We will call equation 7 the theoretical average path law because it is based on a calculated value of the average path.

III. The Average Path Law (experimental expression)

Before we proceed to evaluate expression 7, we shall restate the average path law on the basis of the experimental work of Lind and Bardwell.[1] These investigators have tested expression 5 for the average path by studying water synthesis in a vessel containing a small thin-walled alpha ray bulb in the center. Under these conditions all alpha particles emerging from the central bulb have the same distance to travel through the gaseous mixture. In their second experiment they broke the alpha ray bulb, causing the radon to distribute itself uniformly throughout the gas-mixture. From these experiments they found on the basis of the known fact that chemical reaction is proportional to the path, that for all three sets of alpha particles the average path is

$$\bar{p} = .61\,R \quad (9)$$

They[2] express the total ionization due to the three sets of alpha particles from radon in terms of the ionization per cm. path.

$$I_x = \frac{dI}{dx} = \frac{2}{3}\,\frac{K}{(r - x)^{1/3}} \quad (10)$$

which reduces for $x = 0$ to

$$I_{x=0} = \frac{2}{3}\,\frac{Kr^{2/3}}{r} \quad (11)$$

The ionization due to the alpha particles from Radon is

$$I_1 = N_0(1 - e^{-\lambda t})I_{x=0}\,\bar{p} = \frac{B}{2\rho} \quad (12)$$

Similar expressions are obtained for I_2 and I_3. However we shall make use of the experimental value of the average path of equation 9 (Section VI) and we shall find there that the assumption that 100% Ra A and 100% Ra C decompose on the wall is not supported by experiment. We shall find that 30% (= n) of Ra A and 7% (= m) of Ra C decompose in the gas phase. We now use this result and obtain five equations of the type (12) which when added give for the total ionization

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[1] J. Am. Chem. Soc., **45**, 2585 (1923).

[2] Lind and Bardwell: J. Am. Chem. Soc., **47**, 2675 (1925).

$$I = \frac{B}{\rho}\left[\frac{1}{2} + \frac{n+2}{2}\cdot\frac{1}{3\sqrt[3]{a}} + \frac{m+2}{2}\cdot\frac{1}{3\sqrt[3]{b}}\right] \qquad (13)$$

We shall refer to this equation as the experimental average path law for it is based on the experimentally determined average path. Instead of using the Ionization intensity in stating the average path law we might have corrected equation (7) for the fractions of Ra A and Ra C decomposing in the gas phase in the manner just outlined.

IV. Derivation of Mund's Equation

We shall now briefly indicate a method of derivation of Mund's equations making the same assumptions that he does, but we shall follow the geometrical picture developed in Section I for the deduction of the average path.

Consider $N_o(1 - e^{-\lambda t})$ radon atoms decomposing in time t in a spherical vessel of Volume V. The number N of radon atoms decomposing in the elementary Volume dV located at P (Fig. 1) is

$$N = \frac{N_o(1 - e^{-\lambda t})}{V}\,dV = \frac{N_o(1 - e^{-\lambda t})}{4/3\,\pi R^3}\cdot 2\pi\, b^2 \sin\varphi\, d\varphi\, db \qquad (14)$$

As in section I we have the number dN of radon atoms given by equation (1). From the geometry of figure I it follows that

$$\sin\theta\, d\theta = \frac{b^2 - x^2 - R^2}{2bx^2}\,dx \qquad (15)$$

Instead of calculating now the average path of an alpha particle leaving the point P as was done in section I we shall follow Mund and calculate the total ionization of all the alpha particles decomposing in time t in the whole volume V and subtract therefrom the loss in ionization occasioned by the fact that some of the alpha particles cannot complete their range because they are intercepted by the wall.

The total possible ionization produced by $N_o(1 - e^{-\lambda t})$ alpha particles in time t is when all of them complete their range

$$B = N_o(1 - e^{-\lambda t})\,Kr^{2/3} \qquad (16)$$

The loss in ionization is given similarly by Geiger's law so that the net ionization is

$$I = B - K\int (r - x)^{2/3}\,dN \qquad (17)$$

where the integration extends over the whole volume and over all the possible values of x. Equation (17) is the fundamental relation from which all the cases of interest may be computed.

1.) *Ionization by gaseous radon.*

The ionization in large vessels ($2R > r$) is given by (17) on substituting from (1), (14), and (15).

$$I_1 = B\left[1 - \frac{3}{4R^3 r^{2/3}}\int_o^r\int_R^{R-x}\frac{b^3 - b(x^2 + R^2)}{x^2}\cdot(r - x)^{2/3}\,dx\,db\right] \qquad (18)$$

which on integration yields

$$I_1 = B\left[1 - \frac{9}{20}\rho + \frac{81}{3520}\rho^3\right] \tag{19}$$

The ionization due to gaseous radon in small vessels ($2R < r$) is obtained from (18) by integrating over x with limits from 0 to 2 R. The result is

$$I_1 = B\left[1 - \frac{9}{20}\rho + \frac{81}{3520}\rho^3 - \frac{9}{16}\left(1 - \frac{2}{\rho}\right)^{2/3} \left\{\frac{3}{10}(\rho - 2)^2 + \frac{9}{220}(\rho - 2)^3\right\}\right] \tag{20}$$

2.) *Ionization due to equilibrium amounts of Ra A and Ra C on the wall.*

In the case of a large vessel equation (17) becomes

$$I_2 = \frac{B}{2} - \frac{B}{2r'^{2/3}} \int_{\cos^{-1}\frac{r'}{2R}}^{\pi/2} (r' - x)^{2/3} \sin\theta \, d\theta \tag{21}$$

When the substitutions from (1), (14) and (15) are made and when it is considered that $x = 2R\cos\theta$ when $b = R$ (See Fig. 1) then

$$I_2 = Ba^{2/3}\left(\frac{1}{2} - \frac{3}{20}a\rho\right) \tag{22}$$

In small vessels ($2R < r$) the integration limits in (21) are for θ from 0 to $\pi/2$ and the result is

$$I_2 = Ba^{2/3}\left[\frac{1}{2} - \frac{3}{20}a\rho + \frac{3}{20}\left(1 - \frac{2}{a\rho}\right)^{2/3}\left(a\rho - 2\right)\right] \tag{23}$$

The equations for Ra C are similar to (22) and (23) with "b" substituted for "a."

The expressions obtained here for I_1, and I_2, and I_3 are identical with Mund's equations or are equivalent to them and may be brought into the same form by simple algebraic transformation. The total ionization due to radon, Ra A and Ra C is

$$I = I_1 + I_2 + I_3 = B \cdot F \tag{24}$$

where F is an efficiency factor. Numerical values of F for various values of have been given by Mund.[1] Some of these values are reproduced in Table I, Column 2.

V. Comparison of Average Path Law and Mund's Equation

We may now carry out a comparison of the average path law given in equation (7) and (13) with Mund's equation. To this end we have calculated the quantities which correspond to Mund's F in equations (7) and (13). The results are given in Table I.

[1] J. Phys. Chem., **30**, 892 (1926).

Mund[1] gives the product of ρF in his table and for large values of ρ this product approaches the value 1.10. His equation for ionization as given in (24) may then be written

$$I = B \frac{1.10}{\rho} \tag{25}$$

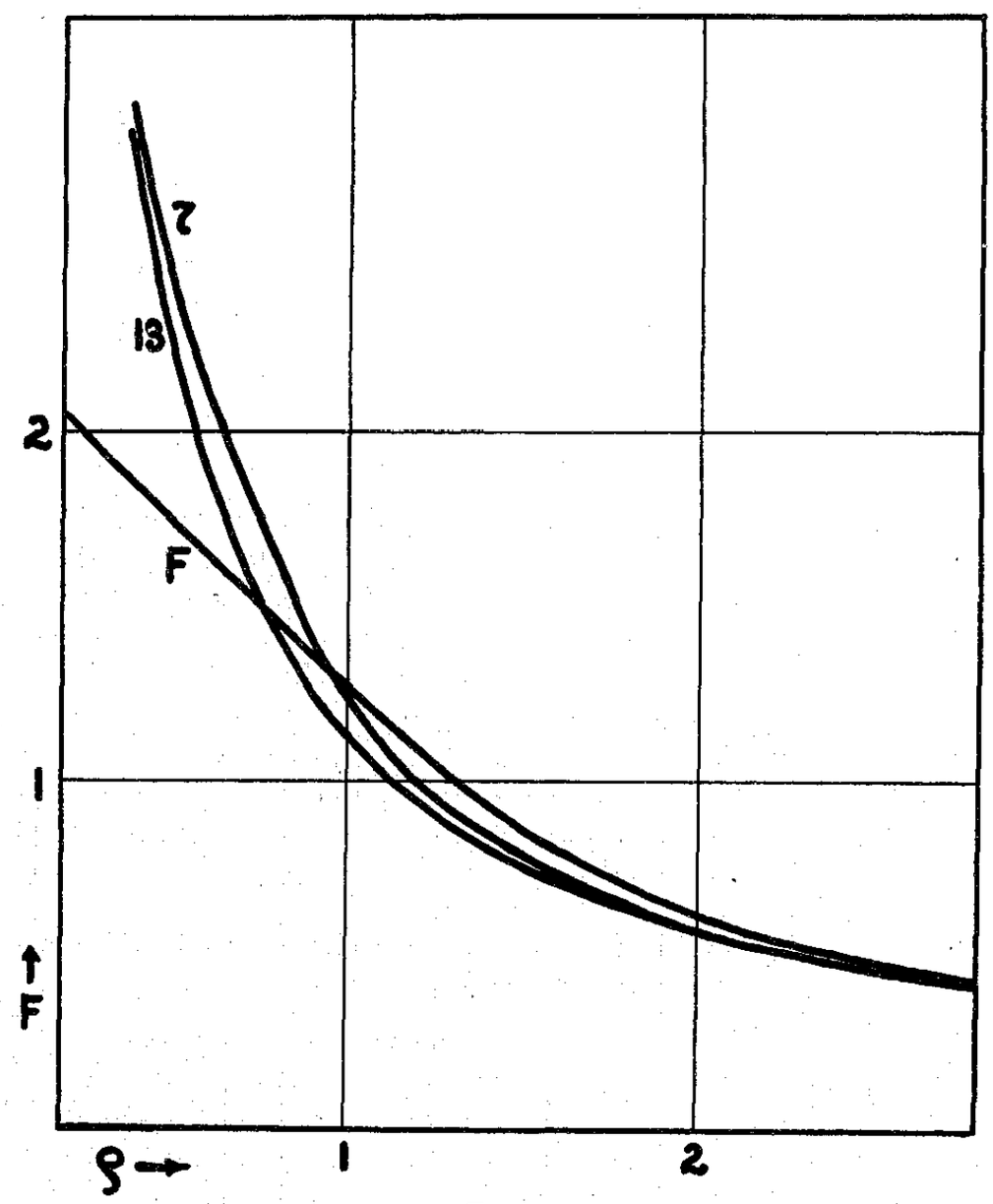


FIG. 2

and we see that this is identical with the theoretical expression of the average path law as given in (8). *For large values of* ρ *(small reaction bulbs) the average path law of Lind and the equations of Mund yield identical results.*

From Fig. 2 it can be seen that for values of ρ up to .8 the two methods yield similar results. But from $\rho = .8$ to $\rho = 0$ which is the region of large reaction bulbs the average path law fails because in this region the average path becomes larger than the ranges of the alpha particles and the average path law must give results which are too large.

[1] J. Phys. Chem., **30**, 892 (1926).

TABLE I

ρ	Mund's F	Equation 7 (Theor. Av. Path Law)	Equation 13 (Expt. Av. Path Law)
.4	1.855	2.940	2.90
.6	1.661	2.156	1.93
.8	1.470	1.669	1.45
1.0	1.283	1.249	1.16
1.2	1.101	1.011	.967
1.4	.946	.851	.828
1.6	.817	.735	.726
1.8	.706	.650	.645
2.0	.621	.579	.580
2.2	.556	.525	.527
2.4	.504	.478	.483
3.0	.391	.379	.387
4.0	.287	.282	.290

Fig. 2 shows these quantities as a function of ρ.

So far we have based our comparison on the theoretical calculations of Lind and Mund. However we can now relate this comparison to the experiments of Lind[1] on water synthesis in vessels of varying size. It was found that the average path law held for small vessels up to 10 cm. in diameter, (air at atmospheric pressure). But we have seen above that Lind's average path law and Mund's relation gave comparable results up to $\rho = .8$ which corresponds to a bulb diameter of 9.9 cm. We see then that the experiments of Lind yield the same result and for vessels of diameter less than 10 cm. either Lind's average path law or Mund's methods may be used to calculate ionization.

VI. Correction of Mund's Equation for the Fraction of Ra A decomposing in the Gas Phase

We have seen above that Mund based the derivation of his equations on the assumption of the validity of Geiger's law and that all of the Ra A and Ra C decompose on the wall. The first assumption is satisfactory but in connection with the second one we wish to point out that Lind[2] has shown that Ra C is not deposited completely on the wall. In a vessel of 2 cm. in diameter he found that 93.3% of Ra C is deposited on the wall and in a vessel of 6 cm. in diameter 88.4% of Ra C is deposited. We will be interested to know what proportion of Ra C would have been deposited in a vessel of 3.5 cm. in diameter. From Lind's experiments it would appear that by proportion 90% of Ra C would deposit on the wall in this case.

Regarding the possibility of Ra A decomposing partly in the gas phase Lind remarks that this would only have a small effect on the ionization as

[1] J. Am. Chem. Soc., **41**, 531 (1919).
[2] J. Am. Chem. Soc., **41**, 531 (1919).

calculated by the average path law. We shall show that this is the case and we proceed to calculate the fraction n of Ra A that decomposed in the gas phase by using the experiemntal expression of the average path (equation 9) in the following manner.

If we consider the sum of the paths of the three sets of alpha particles from radon and the various fraction of both Ra A and Ra C that decompose in the gas phase and on the wall respectively we see that the average value of their path must be equal to the experimental value (equation 9) determined by Lind and Bardwell. That is

$$\frac{1}{3}\left[\frac{3}{4} + \frac{3}{4}\,n + \frac{1-n}{2} + \frac{3}{4}\,nm + \frac{1-nm}{2}\right] R = .61\,R \qquad (26)$$

where n is the fraction of Ra A and m is the fraction of Ra C decomposing in the gas phase. The average path law was tested by Lind and Bardwell in a vessel 3.5 cm. in diameter and taking therefore m = .1 we find from equation (26)

$$n = 29.1\%$$

We may calculate both m and n without using Lind's experimental value of m if we find another equation connecting them. This can be done if we make the following assumption. We consider the process of diffusion or transport to the wall of both Ra A and Ra C. While it is known[1] that the ordinary laws of diffusion do not apply to the process still it seems reasonable to assume that whatever the process may be it is the same for Ra A, and Ra B, and Ra C. We can then say that the fractions of Ra A and Ra C decomposing on the wall are inversely as the average life of Ra A is to the sum of the average lives of Ra B and Ra C:

$$4.4\,n = 67\,m \qquad (27)$$

The average life of Ra A is 4.4 minutes, and the sum of the average lives of Ra B and Ra C is 67 minutes. The assumption made does not seem unreasonable for all these atoms are the products of radioactive change, and they all have nearly the same mass. The number and type of collision that they would suffer in their progress towards the wall would therefore be very similar. If we, for instance consider a certain group dN of these atoms leaving a given point P in the reaction vessel (see Fig. 1) it would appear that they would take about the same time to reach the wall. Since, however, Ra A has a much shorter life than has Ra C (which might also reach the wall while still Ra B) more of the Ra A atoms would decompose on their way to the wall or in the gas phase.

If we now combine equations (26) and (27) we find

$$n = 30.9\% \text{ and } m = 3.5\%$$

These values for n and m check satisfactorily the ones obtained from Lind's experiments cited above.

[1] Debierne: Le Radium, 6, 97-108 (1909).

As far as the purpose for which we need these figures is concerned we may use their average and we will not affect the corrected values for the calculated ionization by more than .2%.

We have therefore calculated the ionization by Mund's equation for the radon, 30% Ra A and 7% Ra C all of which decompose in the gas phase by means of equations of the type of (19) or (20) and for the 70% Ra A and 93% of Ra C which decompose on the wall by equations (22) or (23). The results

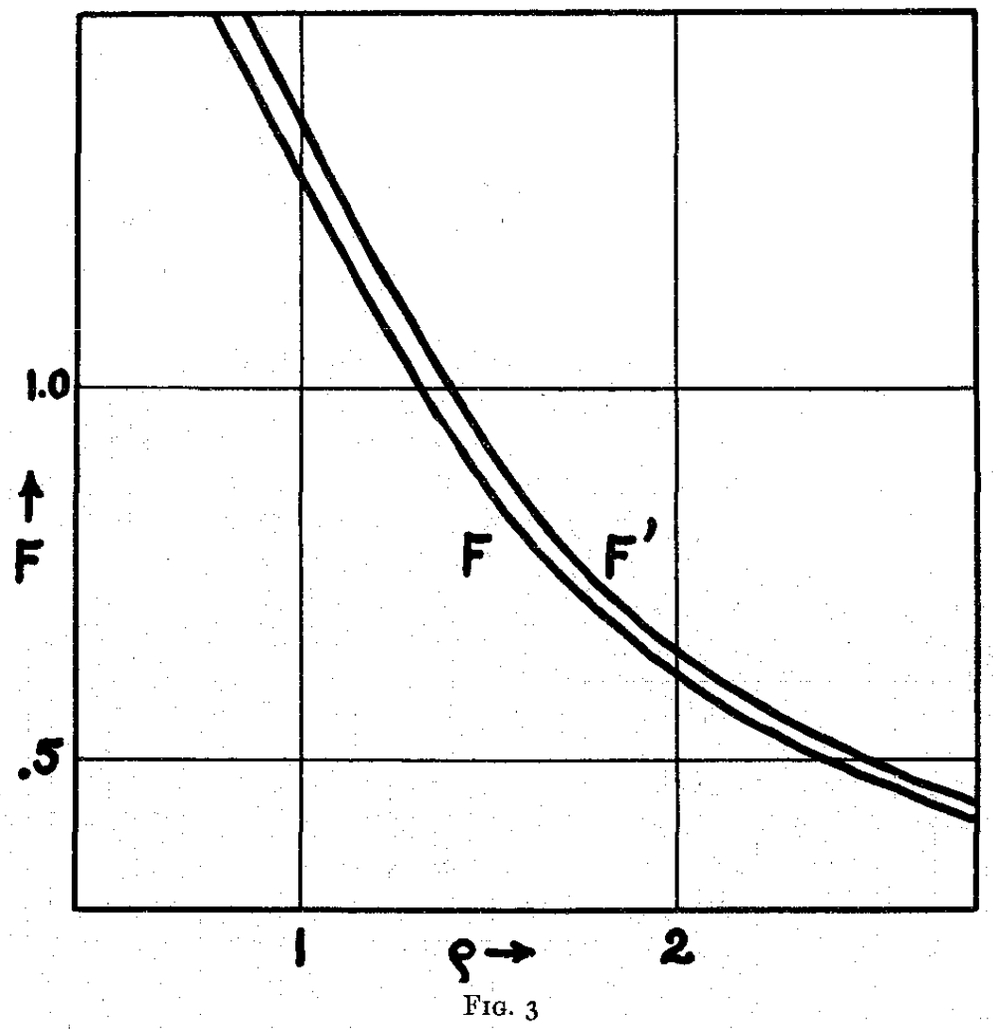


FIG. 3

are given in terms of a corrected efficiency factor and they are summarized in Table II, column 3. For comparison the values of Mund's F factor are also given. Fig. 3 shows these factors as functions of ρ. It is seen that the numerical value of the ionization calculated is increased by about 5%.

While the correction was obtained from experiments of Lind performed in vessels of about 2 cm. diameter, we think that they hold for vessles of somewhat different size, for Lind[1] remarks that the general velocity constant of water synthesis is the same for all sizes of vessels.

[1] J. Am. Chem. Soc., **41**, 541 (1919); **46**, 2003 (1924).

TABLE III

Mund's F when 100% Ra A and Ra C decompose on the wall. F′ when 70% Ra A and 93% Ra C decompose on the wall

ρ	Mund's F	F′	ρ	Mund's F	F′
.4	1.855		1.6	.817	.857
.6	1.661		1.8	.706	.743
.8	1.470		2.0	.621	.647
1.0	1.283	1.357	2.2	.556	.582
1.2	1.101	1.165	2.4	.504	.528
1.4	.946	.996	3.0	.391	.412

It is a pleasure to thank Professor Lind for suggesting this study and for his constant advice and interest.

Summary

We have made a comparison of the ionization produced by radon and its decomposition products as calculated by the average path law and by the method of Mund. The two methods give similar results for small spherical vessels up to a diameter of 10 cm. as has been found previously by Lind by an experimental method.

A new derivation of Mund's equation is given and the assumption made by Mund that all of the Ra A and Ra C decompose on the wall is modified. On the basis of the experimental determination of the average path law by Lind and Bardwell which gives the average path equal to .61 times the radius of the reaction vessel, we have calculated that 30% of the Ra A and 7% of Ra C decompose in the gas phase. We have recalculated Mund's efficiency factor on this basis.

University of Minnesota,
Minneapolis, Minnesota.

13-233 1332

THE CATALYTIC ACTIVITY OF METALLIZED SILICA GELS II. THE HYDROGENATION OF ACETYLENE

BY V. N. MORRIS[1] AND L. H. REYERSON

The hydrogenation of acetylene was one of the projects included in von Wilde's[2] pioneer work on the catalytic hydrogenation of organic compounds. In 1874 he observed that acetylene will unite with hydrogen to give ethylene and then ethane in the presence of platinum black. Several years later, Sabatier and Senderens[3] studied the hydrogenation of this compound in the presence of nickel and copper catalysts. Of the more recent work, that of Ross, Culbertson and Parsons[4] is noteworthy. They found that in the presence of a nickel catalyst it was possible to obtain nearly complete conversion of acetylene to ethylene under proper conditions. That reduction to ethylene may also occur in the presence of colloidal palladium is indicated by the work of Paal and Hohenegger.[5]

The present investigation was undertaken with the primary object of obtaining information regarding the effectiveness of metallized silica gels as catalysts in connection with this reaction. These catalysts, which consist of very finely divided metals reduced at low temperatures within the pores of the adsorptive supporting material, silica gel, might be expected to exhibit properties somewhat different from those of catalysts in the more common forms. The results of x-ray examinations of and adsorption studies with metallized silica gels have recently been reported.[6]

Experimental

The methods and apparatus used in the present experiments were quite similar to those employed by the authors in connection with an earlier investigation, that of the hydrogenation of ethylene.[7] Each catalytic sample used consisted of 3.5 grams of the metallized gel. Each catalyst was kept in a separate catalyst tube throughout the investigation. These tubes were placed side by side in the bath used to maintain temperature control, and were so connected that the gas stream could be directed through any one desired. The tendency towards fluctuations in the compositions of the original mixtures of acetylene and hydrogen was considerably lessened by making use of a saturated solution of sodium chloride as a confining liquid in the aspirating system.

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[1] du Pont Fellow, University of Minnesota, 1925-26.

[2] Von Wilde: Ber., **7**, 352 (1874).

[3] Sabatier and Senderens: Compt. rend., **128**, 1173 (1899); **130**, 1559 (1900).

[4] Ross, Culbertson and Parsons: J. Ind. Eng. Chem. **13**, 775 (1921).

[5] Paal and Hohenegger: Ber., **48**, 275 (1915).

[6] Reyerson and Swearingen: J. Phys. Chem., **31**, 88 (1927); Reyerson, Harder and Swearingen: **30**, 1624 (1926).

[7] Morris and Reyerson: J. Phys. Chem., **31**, 1220 (1927).

The particular platinum catalyst used was reduced originally by means of adsorbed hydrogen at a temperature of about − 20°. Prior to its being used in catalytic studies, it had been given an additional treatment with hydrogen at 100°. The palladium catalyst was reduced originally in similar fashion and had also been given additional treatments with hydrogen at higher temperatures.

The acetylene was prepared by the action of water on calcium carbide. The removal of the most deleterious impurities, phosphine and hydrogen sulfide, was accomplished by using the method of Berge and Reychler.[1] The gas was stored over water in a large bottle. The freshly prepared gas was absorbed by bromine to the extent of 97.6 per cent.

The electrolytic hydrogen used was passed through a purification train containing solutions of pyrogallate, permanganate and sulfuric acid. Its purity, as determined by the explosion method, was 96 per cent.

Although the determination of the acetylene and hydrogen in the original mixtures presented no difficulties, the same was not true for the analyses of the effluent gases. These latter contained not only acetylene and hydrogen, but also the reaction products, ethylene and ethane. Several methods for distinguishing between ethylene and acetylene were tried before that of Ross and Turnbull[2] was adopted. According to the method of these authors, acetylene may be determined in the presence of ethylene by titrating the nitric acid liberated by the reaction of the former gas with a solution of silver nitrate. This reaction is represented by the following equation:

$$C_2H_2 + 3AgNO_3 \longrightarrow C_2Ag_2.AgNO_3 + 2HNO_3$$

The total unsaturated gas may be determined in another sample by absorption in bromine, and the ethylene thus obtained by difference.

Since a considerable decrease in volume accompanies the reactions, and the change in volume in one case is often much greater than in another, the tabulation of the actual percentages of the various substances in the mixtures before and after catalysis does not give a very clear indication of the extent to which reaction has taken place. Although an equation for calculating the percentage conversion was developed, there appeared to be so many possible sources of error in employing it that the results obtained by its use have not been recorded.

Results

At the time the experimental work was carried out, it was thought that decomposition and polymerizations of the acetylene took place only to a small extent. Since there appeared to be no violent heating of the catalysts, nor any evidence of the formation of liquid hydrogenations (such as were reported by Sabatier and Senderens[3] when using nickel and copper catalysts no analyses were made for any products other than ethylene and ethane. In reviewing the results of analyses, it appears to be highly probable that other products

[1] Berge and Reychler: Bull., **17**, 218 (1897).
[2] Ross and Turnbull: J. Am. Chem. Soc., **41**, 1180 (1919).
[3] Sabatier and Senderens: Compt. rend., **128**, 1173 (1899); **130**, 1559 (1900).

were formed in certain cases, since the volume of that gas which escaped detection in the analytical procedure followed was often increased by passage over the catalysts to a much greater extent than could be explained on the basis of the changes in volume which accompany reaction. Any liquid or solid products formed could easily have escaped detection by being held in the silica gel.

Effect of Variation of the Temperature. During the study of the effect of variation of the temperature, the rate of flow of the exit gases was approximately 60 cc. per minute. New mixtures of acetylene and hydrogen were made up each time the temperature was changed. Although the attempt to have all the mixtures of approximately the same composition was not entirely successful, the ratio of hydrogen to acetylene was always somewhat greater than that theoretically required for the formation of ethane. The experimental results are shown in Table I.

TABLE I

The Effect of Variation in Temperature on the Hydrogenation of Acetylene.

		Comp. of the original mixture		Comp. of the Final Mixture			
Temp.	Catalyst.	C_2H_2 %	H_2 %	C_2H_2 %	H_2 %	C_2H_4 %	C_2H_6 %
0°	Pd	27.4	66.1	23.6	64.8	0.3	1.1
50	Pd	24.8	66.2	0.5	34.2	15.5	26.7
100	Pd	20.2	67.6	2.9	59.8	2.8	18.3
0°	Pt	27.4	66.1	24.0	66.3	2.7	0.4
50	Pt	24.8	66.2	21.9	61.2	1.7	1.7
100	Pt	20.2	67.6	1.6	49.1	6.1	19.7

In addition to platinum and palladium, a copper catalyst was also tried. At 100°, it exhibited little if any activity. At 200° it proved to be a fairly good catalyst for the production of ethane. None of the catalysts were effective at 0°: palladium was active at 50° and above; platinum at 100°; and copper at 200°.

Palladium and platinum tend to catalyze the formation of both ethylene and ethane in general. The production of ethylene is quite interesting, particularly in view of the fact that hydrogen more than sufficient for the formation of ethane was always present. For some reason the production of ethylene in the presence of palladium at 100° was much less than at 50°. An attempt to repeat this run latter led to rather inconclusive results, as the mixture made up was not the exact duplicate of that used in the original experiment.

Effect of Variation in the Reaction Mixture. In the investigation of the effect of variation in the composition of the reaction mixture, the temperature was maintained at 100°, and the rate of flow of the exit gases at 30 cc. per minute. The results are shown in Table II.

TABLE II

The Effect of Variation in the Reaction Mixture on the Hydrogenation of Acetylene.

Catalyst	Comp. of Orig. Mixture C_2H_2 %	H_2 %	Comp. of Final Mixture C_2H_2 %	H_2 %	C_2H_4 %	C_2H_6 %
Pd	8.2	80.2	0.5	56.8	2.6	10.1
Pt	8.2	80.2	0.0	61.5	0.2	11.1
Pd	18.4	70.5	1.8	53.6	8.6	9.7
Pt	18.4	70.5	0.0	51.3	2.3	16.6
Pd	38.0	52.7	9.5	31.6	31.3	1.2
Pt	38.0	52.7	8.1	46.8	24.3	1.3
Pd	47.2	41.3	31.9	21.4	27.0	7.3
Pt	47.2	41.3	42.9	25.7	12.1	7.5
Pd	65.2	22.0	62.2	6.4	10.0	1.3
Pt	65.2	22.0	64.7	14.4	3.0	2.3

Discussion

There are certain obvious differences in the behavior of palladium and platinum as catalysts. Palladium appears to be the better catalyst for the production of ethylene, regardless of the original mixtures used. Platinum, on the other hand, is somewhat more effective from the standpoint of the production of ethane. Platinum appears to catalyze the more complete total hydrogenation of the acetylene when the hydrogen is in excess, but palladium is more effective when the acetylene is in excess.

The most interesting information contained in Table II has to do with the availability of these catalysts for the production of ethylene by the hydrogenation of acetylene. The ratios of ethylene to ethane, resulting from the catalysis of the reaction in the case of a mixture containing orginally 37.9 per cent acetylene and 52.7 per cent hydrogen, compare very favorably with the best ratios of these two products obtained by Ross, Culbertson and Parsons[1] after a rather thorough study of the use of nickel as a catalyst for this reaction in a static system. On account of the greater excess of hydrogen and the larger amount of impurities in the gases used in the present work, the actual percentages of ethylene in the resulting mixtures were not as high as those obtained by these investigators. In view of the favorable results already obtained, it appears that a further investigation, having as its purpose the determination of the best conditions for the production of ethylene from acetylene in the presence of platinized and palladized gels, should yield gratifying results.

An interesting point in favor of the use of silica gel as a supporting material can be made after comparing the present procedure with that followed by

[1] Ross, Culbertson and Parsons: J. Ind. Eng. Chem., 13, 775 (1921).

Ross, Culbertson and Parsons. These investigators found that ethane was the almost exclusive product of the reaction unless the catalyst were given a very special treatment. On account of the strong tendency of nickel to adsorb hydrogen, a satisfactory yield of ethylene was only obtained after repeated treatments of the nickel catalyst with acetylene, which latter gas gradually tended to displace the adsorbed hydrogen. Even after this treatment it appears probably that the catalyst could not have maintained its activity for ethylene formation in a dynamic system.

With metallized silica gels, on the other hand, this laborious treatment of the catalysts is not necessary, ethylene being readily produced when the proper mixtures are passed over the catalysts. Although platinum and palladium adsorb hydrogen as a rule at least as strongly as does nickel, the gel itself undoubtedly has a much stronger adsorption for acetylene than for hydrogen, and as has recently been pointed out by Rideal and Taylor,[1] "it is possible that one of the functions of a support material is to provide the catalyst with a reservoir of one or more of the reactants." In view of the fine state of subdivision of the metals in metallized gels, it does not appear to be unreasonable to assume that the adsorption by the silica adjacent to active metal atoms may have an influence on the progress of the catalytic reaction. The adsorptions of acetylene by the metallized gels have not been measured.

This seems especially plausible if the assumption is made that reaction results only when an acetylene molecule comes in contact with a hydrogen molecule adsorbed by the active catalytic centers. The results of this investigation are not complete enough to support this view definitely; but the evidence points strongly in that direction. If the above assumption is made, then of course the ethylene first produced must strike another hydrogen molecule adsorbed on the surface before ethane is formed. The results given in Table II tend to confirm this assumption. From kinetic considerations it is evident that when the partial pressure of hydrogen is high as compared to acetylene then the number of acetylene molecules striking the hydrogen molecules already on the catalytic surface will be small compared to the number of hydrogen molecules reaching these same points. Reaction under the conditions of the above experiments would then be rather small. With an increase in the partial pressure of acetylene the chance of an acetylene molecule striking a hydrogen molecule already adsorbed by the catalyst would be materially increased. This would be the case even though the hydrogen molecules were as yet more successful in the competition for any uncovered areas of the catalytic surface. However, as the percentage of acetylene in the gas mixture increases the acetylene molecules will be more and more successful in reaching the uncovered areas. They will no doubt be much more strongly adsorbed so that finally the total active area of the catalyst will tend to be covered by acetylene molecules and reaction will practically cease. The results obtained in these experiments indicate that the above assumptions give a reasonable picture of the mechanism of the reaction. Additional experiments are planned in order to further confirm the above point of view.

[1] Rideal and Taylor: "Catalysis in Theory and Practice," 122 (1926).

Summary

Both ethylene and ethane are produced during the hydrogenation of acetylene in the presence of metallized silica gels. As the temperature is raised, the metals become effective catalysts in the following order: palladium, platinum, and copper. As the ratio of acetylene to hydrogen in the original mixture is increased from about 1 to 10 up to 3 to 1, the production of ethylene goes through a distinct maximum. It appears to be probable that the combined adsorptions of gel and metal produce a more satisfactory condition for the catalysis of the formation of ethylene than would the adsorption of either alone.

School of Chemistry,
University of Minnesota,
Minneapolis, Minnesota.

PHOTOSYNTHESIS WITH AMMONIA

BY DEAN BURK

The present paper[1] reports photochemical experiments attempting (1) to induce ammonia to build up complex biochemical nitrogen compounds with carbonic acid, formaldehyde, glucose, and other carbonaceous substances; (2) to reduce carbonic acid, bicarbonates, and carbonates; and (3) to oxidize ammonia to hydroxylamine, nitrites, and nitrates. Sunlight in combination with colored catalysts was used, and the experimental conditions, particularly of temperature and illumination, were made to correspond as closely as possible to the ordinary conditions of plant growth. The work is a natural sequence to the researches of Baudisch,[2] Baly,[3] and Spoehr,[4] their coworkers, and others, who have worked along similar lines, using chiefly ultra violet light, and who have obtained suggestive results as to the mechanism of photosynthesis in plants. The one serious criticism to be made of the important work of these investigators is that the ultra violet light region in the spectrum of sunlight is neither wide nor intense, nor does it extend to the very short wave lengths, thus limiting any direct application of their results to plant phenomena Furthermore it is known that plants may grow normally either in (1) sunlight which has passed through glass, which removes all but about five hundred Ångström units of the sun's ultra violet light; or (2) artificial light which contains no ultra violet light. In all of the writer's experiments exposures were made behind glass vessels, the thickness of the walls of which varied from five to ten hundredths of a millimeter.

The question of the effect of long wave ultra violet light (330 $\mu\mu$ to 390 $\mu\mu$) upon plant growth as a whole is still unsettled,[5] as is indeed also, the question

[1] A brief résumé of a dissertation submitted by the writer in partial satisfaction of the requirements for the Degree of Doctor of Philosophy at the University of California, May 1927. In nearly all the work on photosynthesis reported previously, the experimental conditions have not been described with the detailed precision which the subject demands, and in addition, it has not been apparent always that such detailed data were available. The present discussion is based upon a mass of detail which would be impracticable to publish, but which may be found in its entirety in the dissertation.

[2] Naturwissenschaften, 1914, Heft 9, 10, and many other papers.

[3] J. Chem. Soc., **119**, 1025 (1921); **121**, 1078 (1922); **123**, 185 (1923); J. Ind. Eng. Chem., **16**, 1016 (1924).

[4] Biochem. Z., **57**, 110 (1913); Plant World, **19**, 1, (1916); J. Am. Chem. Soc., **45**, 1184 (1923).

[5] It would be well to make mention of a common misconception among plant physiologists. Some believe that by passing sunlight through window glass, as might be done in a greenhouse, that all the ultra violet light is removed. Such is not the case. Ordinary glass transmits wave lengths as short as 330 to 340 $\mu\mu$ (and sometimes even shorter), and since the visible rays end at 380 to 390 $\mu\mu$, there are thus some 40 to 50 $\mu\mu$ (400 to 500 Ångström units) of ultra violet light which may be transmitted. In temperate zones the ultra violet region does not extend much beyond 300 $\mu\mu$ (290 $\mu\mu$ in India) and ordinarily not beyond 310 to 320 $\mu\mu$. Furthermore, the region 310 to 330 $\mu\mu$ is very much less intense (one half to one tenth) than the region 370 to 380 $\mu\mu$, so that it may be stated safely that glass transmits not only 60 to 80% of the ultra violet wave length region, but also that the actual amount of energy transmitted as ultra violet light is even greater than these values. It is true that these figures (which err, if at all, on the side of conservatism) depend somewhat upon the intensity of the light, and the thickness, age, and cleanliness of the glass, but in general, variations in these factors can make little difference in the conclusions. On the other hand, it is well to bear in mind that passing bright sunlight through glass may remove the rays 300 to 330 $\mu\mu$ and that these particular rays may happen to be those ultra violet rays which affect organic substances in particular reactions, while the rays 330 to 390 $\mu\mu$ may be relatively ineffective.

of the effect of infra red light. Upon the basis of numerous, but from the modern point of view, insufficiently critical experiments, Daubeny[1] and Draper[2] were the first to deny the *essentialness* of either of these kinds of invisible light.[3] Furthermore, these workers were able to establish the incorrectness of the prevailing view of the previous sixty years, which derived initial support from the experiments of Senebier,[4] namely, that the violet and chemical rays were the most powerful rays of sunlight for the growth of plants. But so far as the writer knows, the first and only experiments concerning the *essentialness* of invisible light for plant growth to be carried out in a manner long hoped for by plant physiologists, have been performed within the last year or two at the Boyce Thompson Institute for Plant Research by Popp.[5] For the first time, presumably, many species of higher green plants have been grown somewhat extensively over their entire growth period in differently colored sunlights, both the intensities and wave length compositions of which were simultaneously and accurately known and controlled. From all the criteria used Popp could find no significant changes resulting from growing plants in light from which wave lengths shorter than 389 $\mu\mu$ has been excluded. Numerous changes, however, were observed when parts of the visible spectrum (i.e. wave lengths less than 529 $\mu\mu$ or even 427 $\mu\mu$) were excluded.

In 1779 Sir Humphry Davy[6] made the first attempt to reduce carbonic acid artificially without the aid of plants, by means of sunlight, and similar attempts have been made ever since, often in the presence of both inorganic and organic catalysts. Within the last few years success with inorganic catalysts and sunlight has been claimed by Moore[7] and Dhar and Sanyal.[8] Moore claimed that in the essential presence of ferric chloride, carbon dioxide and water could be reduced to formaldehyde. Dhar and Sanyal, who used tropical sunlight, now dispute Davy's results and claim that no catalyst at all is necessary, adding that "we are of the opinion that the intensity and prolonged exposure have much to do with this photosynthesis of formaldehyde in sunlight." They make no mention of the fact that their results contradict seemingly the Grotthuss-Draper First Law of Photochemistry that "only those rays that are absorbed produce chemical change." According to Aschkinass,[9] some one hundred and fifty feet of water are required to reduce by absorption either the blue, green, or yellow, rays to .37 their initial intensity. Porter and Ramsperger[10] have recently pointed out the need for the complete

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[1] Phil. Trans., **126**, 149 (1836).

[2] Phil. Mag., **23**, 161 (1843).

[3] Am. J. Bot., **13**, 706 (1926).

[4] Mémoires Physico-Chimiques, Geneva, 1782.

[5] The infra red rays, be it recalled, were discovered first by Sir William Herschel in 1800 (Phil. Trans., **1800**, p. 255), and the ultra violet rays first by Ritter (Gilb. Ann. Physik., **12**, 408, 1803) and Wollaston (Nicholson's Journal, **8**, 293, (1804)) simultaneously in 1801.

[6] Beddoes: "Contributions to Science," 161.

[7] Biochemistry, (1921).

[8] J. Phys. Chem., **29**, 926 (1925).

[9] Wied. Ann., **55**, 401 (1895).

[10] J. Am. Chem. Soc., **47**, 79 (1925).

absence of organic matter in the experimental vessels. It is not apparent that Dhar and Sanyal took this precaution, and the view that the formaldehyde they obtained was derived from organic matter is strengthened inferentially by the fact that whereas one hour's exposure in open vessels was sufficient to allow detection of traces of formaldehyde, ninety hour's exposure were required in sealed tubes, in which no atmospheric dust could accumulate.

Experimental

Methods of Exposure.

The distinctive feature of the writer's technique, which should be kept in mind when comparing it with that of others, was the use of condensed light. The employment of lenses was found to be desirable, indeed indispensable. The lenses were large, spherical, colorless, common-glass flasks twelve to sixteen inches in diameter filled with clear water, and mounted on stationary iron tripods; at times, small four and one half inch plano-convex glass lenses were used also. Calculations indicated that the intensity of sunlight could be increased to a maximum of approximately five thousand fold; for noon sunlight this would be about five million times the intensity of an ordinary forty watt house lamp. The increase in total intensity was considered not to be so advantageous or to be desired particularly, as was the increased intensity of particular lines, perhaps rather weak in normal sunlight, which might be instrumental in causing certain photosynthetic reactions. It was estimated that exposure behind one of these lenses on a clear day was equal, as regards the amount or total calorific value of the light, to exposure to ordinary light for a month of clear days; experiments sustained this assumption. It may be mentioned that the ordinary ultra violet mercury lamp has a total energy yield about equal to good sunshine. And so, since these experiments were conducted with intensities of light which have been used seldom before, the hope was entertained that either of two effects might be observed; (1) that the rate of reaction would be increased more than linearly with a linear increase in intensity, as has been observed to a small extent in the hydrogen chlorine reaction, where the rate of reaction divided by the intensity is slightly greater at greater intensities; or (2) that new photochemical reactions would take place only above certain critical intensities or photochemical threshholds. It may be stated here that neither of these hopes was realized; although it is possible still, that the intensities used were not high enough. There are other advantages to the use of these lenses, and practically no disadvantages. For instance, it might be imagined that their effect would cause difficulties, but a simple water bath can keep the temperature of the exposed solution below 30°C. It is true that over a small localized area, such as a few square microns, the temperature might become slightly higher than presumed, but this could be true of ordinary sunlight also. Dhar and Sanyal stated that results obtained at one time of year were difficult to repeat at other times. The writer has had no such experience, presumably because of his continuous use of condensed light.

It cannot be objected that the great intensities used could be harmful, or shield results, because the beam of focused light never covered the whole

surface possible, but generally one tenth only or less. The products formed could be removed to relatively unilluminated parts of the exposed tube, where they would not be decomposed further by the intense light. This condition has the same good effect as that which Baly obtains when he shakes the chambers he is exposing to ultra violet light, thus carrying the primary products of the reaction to the back of the chamber out of danger of further decomposition.

The use of lenses is by no means without example in plant processes. It may be stated, with considerable assurance, that the active concentration or intensity of photosynthesizing light inside any particular plant under observation can never be known; the plant is a veritable nest of lenses. First, the external cells of the leaves of many plants have been observed to function exactly like convex lenses, the light entering them being forced to a focus before being used; this is well illustrated in the case of cells of *Schistostega osmundacea* which grow in weak cave light, the chloroplasts forming an aggregate at the back of the cell where the light intensity is the highest. Second, the chloroplasts themselves are almost perfect double convex lenses. Finally, every fat globule or other similar heterogeneous phase in the protoplasm is found quite generally to have the approximate shape of a lens. These instances are mentioned not because the writer believes that these natural lenses bring about some unobserved or unaccounted for effect in plants (indeed, one might fear harm, especially in brilliant sunlight), but to show plainly that in using lenses he was not making use of some advantage not possessed by plants. There is no question in his mind that these natural lenses do actually increase considerably the intensity of the light inside the plant.

The exposed solutions were made up with water twice distilled which had a conductivity not greater than 5×10^{-6} reciprocal ohms. Baker's C. P. chemicals without further purification were nearly always employed. Most of the solutions were exposed in glass bulbs blown on the end of common soft-glass tubes about a foot in length and twelve millimeters in diameter. The bulbs were quite spherical, had a capacity of fifteen to sixty cubic centimeters, were just as thin as safety would allow (from five to ten hundredths of a millimeter), and were very transparent. In most of the experiments the tubes were sealed, often under vacuum. In some of the experiments they were not sealed, in order to observe what effects the constituents of the atmosphere might have. The unsealed tubes were protected by hoods of loose tin foil bent over in such a manner as to allow free entrance of air but to exclude foreign matter. Exposures were made on top of a roof, several blocks away from any laboratory which might give off undesirable fumes. The tubes were always cleaned with chromic acid at 100° C, followed by hot alcoholic potash, hot concentrated nitric acid, many rinsings of distilled water (which effectively removed all nitrates), and then were dried at 100° C and put away until used. By means of suitable supports an exposed tube was held dipped in a liter beaker of water in such a manner that the bulb part of it was about an inch under water and in the direct path of the focused beam of light. The focal point, at which the highest intensity of light would be

obtained, was never used ordinarily. The beam was usually one quarter of an inch or more in width at the point where it entered the bulb. The position of the bulb required changing every twenty minutes. No heliostat was employed. The tubes were exposed to lenses for four to six hours a day, but they also received the ordinary sunlight, direct and diffuse, throughout the entire day. A battery of twenty lenses and tubes was generally kept in operation. Exposures were continued from one day to two weeks, depending upon the nature of the experiment and the speed with which tubes could be prepared for exposure and analyzed subsequently. Many miscellaneous photochemical reactions were observed and in all cases three days' exposure to lenses, equal to three months' exposure to ordinary light, sufficed to approach closely the equilibrium or stationary state. The tubes were prepared most often in duplicate. One was exposed, while the other, as a control, was wrapped heavily in tin foil, so as to exclude light entirely, and placed alongside the first in the same thermostat. This system of maintaining controls was ideal; any difference between the two tubes appearing upon examination could be considered immediately as being the result of either primary or secondary effects of radiant energy.

Methods of Analysis.

The methods used to analyze the different exposed solutions and their respective controls varied widely, and it would be impossible to give here more than a list of most of the tests used quite generally, and to add that on the average each exposed solution was examined by about twenty five different tests. Most of the tests were performed as described in Mulliken,[1] but changes and improvements were sometimes necessary. The sensitiveness of each test, as carried out either in distilled water or in the experimental solutions, was always known. The sensitiveness of the majority of tests ranged from one to fifty parts per million by weight, although several, notably Schryver's, Griess, and Trommsdorff were considerably more sensitive. It should be understood that when negative results were obtained with unknown solutions, traces of the substance being examined for were added to the unknown solution and the test repeated, in order to insure correct interpretation. The pH was often adjusted to neutrality before testing. Where the solutions contained inorganic catalysts they were either distilled first, or examined directly, with or without filtering. In the following list of tests attention needs to be called to the fact that each reagent is usually a test for many other substances besides those specifically mentioned, and hence trustworthy conclusions should obtain when a whole series of tests is performed on a solution, with negative results: reduction of permanganate, mercuric oxide, silver nitrate, and Tollens' reagent for formic acid, hydroxylamine, etc.; Schryver's, resorcin, and gallic acid tests for formaldehyde; Schiff's reagent for aldehydes in general; Molisch test for carbohydrates; Prussian Blue test for nitrogen, cyanide; Fehling's test for reducing sugars

[1] "A Method for the Identification of Pure Organic Compounds." 3 vols. (1904, 1911, 1916).

and formaldehyde; Benedict's tests (second modification) for reducing sugars, but not formaldehyde; Pierart's, Barfoed's, dilute iodine solution, saccharimeter, and aniline acetate paper pentosan tests for various carbohydrates; the various reagents for proteins and alkaloids (Millon's, xanthoproteic, Biuret, mercuric chloride, picric acid, phosphotungstic acid, etc.,) Rimini, Simon, potassium ferrocyanide, carbylamine, Nessler, concentrated iodine in potassium iodide, formaldehyde and concentrated iodine in potassium iodide (Thatcher's test), sublimation of solids (darkening, melting, odor, burning of sublimate, residue) tests for the various amines and nitrogen bases; diphenylamine, brucine, Griess, powdered zinc and Griess, Trommsdorff tests for oxygen nitrogen compounds and oxidizing agents (i.e. hydrogen peroxide, chlorates, chlorine, ferric ion, etc.,); potassium ferricyanide, potassium ferrocyanide, and potassium thiocyanate for ferrous and ferric ions; organic solvent extractable and precipitable fractions. The pH, titration values to various pH's, titration values with N/20 and N/200 permanganate, color and odor were usually noted. Various forms of nitrogen were measured quantitatively by the modified Gunning-Kjeldahl method, Devarda method, Van Slyke method, distillation in alkali at 100° C, vacuum distillation in dilute alkali at 40 to 45° C, vacuum distillation in dilute acid at 40 to 45° C.

Statement and Discussion of Results.

A good portion of the work was concerned with hexamethylenetetramine, $C_6H_{12}N_4$, a weak mono-acid base which hydrolyses in water according to a second order reaction and at a rate depending upon the concentration, pH, and temperature, to give six molecules or formaldehyde and four molecules of ammonia. This substance can be obtained easily in a highly purified state and by adjusting properly the pH with sodium hydroxide and sulfuric acid any desired equilibrium concentration of formaldehyde may be obtained. A highly buffered range exists between pH 7.4 and 4.0. The whole range of concentrations was used, with and without catalysts.

In one of the earliest experiments without catalysts, in which the technique of exposure differed from that described already, 300 cc. of .8 M hexamethylenetetramine (or, expressed in terms of the hydrolyzable constituents 4.8 M formaldehyde and 3.2 M ammonia) were exposed in a sealed Jena glass flask over a period of 54 days to cloudless sunlight for 210 hours, and to 68 hours of sunlight condensed by simultaneous reflection from a maximum of thirty silver mirrors through glass lenses four and one half inches in diameter. The most exhaustive analysis could detect no difference between either this or similarly exposed tubes and the respective controls. Owing to the amount and duration of radiant energy supplied it would be difficult to make a more effective demonstration of the Grotthuss-Draper law. A significant fraction of the infra red was absorbed, no doubt.

When catalysts were used (and the methods of exposure described initially, employed) the usual range of concentration was from .1 to 1%, but much smaller and larger amounts were often employed. Ferric tartrate,

sodium citrate, potassium permanganate, copper sulfate,[1] magnesium ribbon and ferrous sulfate, yellow mercuric oxide, and a compounded mixture of equal parts by weight of the sulfates of ferric, ferrous, magnesium, manganese, and copper and also ferric oxide were tried. Entirely negative results were obtained, with the following minor exceptions. The ferric tartrate and potassium permanganate decomposed photochemically after about a day's exposure to lenses to give ferrous ion and manganese dioxide, and also presumably carbonate, since no formic acid was found. Traces of nitrates (1 p.p.m.) were found often when ferric ion was present. When free acid existed along with hexamethylenetetramine, i.e., when the pH was greater than 4, small amounts of formic acid and a primary amine (methylamine presumably) were produced thermochemically after a week's standing at a maximum temperature of 30° C. The amounts obtained were neither increased nor decreased by the presence of either catalysts or light, and the reaction observed was no doubt that described by Werner,[1] who worked at somewhat higher temperatures (50 to 110° C), but for much shorter periods of time. At 50 to 60° C relatively large amounts were obtained by the writer after 24 hours. Dhar and Sanyal stated that when the system NH_4OH, CO_2, HCOH, was exposed for twenty hours, methylamine was produced. In the absence of experimental details, particularly in regard to controls, it would be difficult to criticize this observation, but suffice to say that the writer believes that if enough carbon dioxide had been present to yield a pH of less than 7, and if the temperature was not kept below about 40° C, or even less, the reaction observed was thermochemical, probably. With mercuric oxide, which was used up in the reaction, formates, carbonates, nitrates, and nitrites were produced photochemically but not thermochemically. The amount of nitrites and nitrates formed depended greatly upon the ammonium ion concentration, and was related closely to the amount of surface rather than bulk of mercuric oxide used. The relative amount of nitrate to nitrite apparently increased with length of exposure, although no special experiments were made to determine whether mercuric oxide would oxidize photochemically nitrites to nitrates. Experiments with identical results were made with ammonium salts, as well as with hexamethylenetetramine.

Moore claimed that all substances of biological origin yield formaldehyde upon exposure to sunlight. Plausible theoretical schemes for the building up of plant protein compounds directly from glucose and ammonia, without going through nitrate, nitrite, or formhydroxamic acid steps have been sug-

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[1] Two miscellaneous reaction may be mentioned. Very pure metallic copper may be prepared by the photochemical reduction of copper sulfate organic acid solution, providing alkali is absent. When alkali is present, as in Benedict's or Fehling's solutions, copper is not produced in quantity until the reduction (to cuprous oxide) has been about completed. Sodium nitrite and methyl alcohol, in either the presence or absence of copper sulfate at the time of exposure, were observed to yield rapidly a nitrogeneous organic acid, the copper salt of which was insoluble in water. Formhydroxamic acid or an isomer had been produced no doubt, according to Baudisch, but time did not allow further study and adequate identification.

[2] J. Chem. Soc., **111**: 2, 844 (1917).

gested.[1] Experiments of the writer do not lend support to either of these views. Vacuum sealed solutions of widely varying concentrations (600 fold) of the purest glucose obtainable, with and without ammonium chloride, ferric chloride, and ferrous sulfate present also, at varying hydrogen ion concentrations (pH 3 to 7.5), were exposed to condensed light for 70 hours over a period of two weeks. Saccharimeter readings were made when the concentrations of glucose permitted. All of the numerous tests mentioned previously were employed to detect photochemical change, but no indication of the formation of any new organic substances was obtained. Most of the ferric ion was reduced to ferrous ion, after a time, of course. It is a criticism of these experiments, perhaps, that oxygen gas was excluded. The hypotheses of Stewart and the statement of Moore were formulated, however, without reference to oxygen.

Dhar and Sanyal reported that they obtained reducing sugars from formaldehyde when exposed to tropical sunlight in the essential presence of ferric chloride or methyl orange. This result was not confirmed by the writer. Solutions of vacuum redistilled, colorless formaldehyde at three different concentrations (15, .6, and .024%) were exposed in the presence of ferric chloride at three different concentrations (2, .02 and 0%). 2 and 0% ferrous sulfate were also tried. The solutions were made up with redistilled water, sealed under vacuum, and exposed to 35 hours of condensed sunlight over a period of two weeks. The pH was varied from about 2 to 7.5. The ferric ion was reduced photochemically to ferrous ion, the rate depending a great deal upon the pH. No reducing sugars, pentoses, other carbohydrates, or odorous substances were produced.

Carbon Dioxide Reduction.

Ammonium carbonate is what might be termed the ideal plant nutrient; not so much because it supplies the four main essential elements, but because these four main elements are in those two radicles, carbonaceous and nitrogenous, which are most rapidly absorbed and efficiently used by plants. While nitrate enters rapidly, the general concensus of opinion and experimental findings is that ammonium ion enters even more rapidly. That ammonium ion is used more efficiently than nitrate is not surprising, since it is the form in which nitrogen appears in the plant. Nitrate would have to be reduced, at an expense of energy.

The ammonium carbonate used was Baker's $(NH_4)_2CO_3NH_4CO_2NH_2$. Ammonium formate was used also. Formic acid is the first reduction product of carbonic acid (i.e., dihydroxyformic acid), and results might perhaps be obtained with formate rather than carbonate, although it is to be remembered that much more energy is needed to reduce formic acid to formaldehyde than carbonic acid to formic acid[2] (about five times). Spoehr[3] has stated that he

[1] Stewart: "Recent Advances in Organic Chemistry," 258 (1918).

[2] See in this connection the relations existing if hydrogen gas were involved, in a paper by the writer "The Free Energy of Nitrogen Fixation by Living Forms," J. Gen. Physiol., 10, 566 (1927).

[3] Biochem. Z., 57, 95 (1913).

tried for years in many different ways to reduce formic acid to formaldehyde by means of radiant energy, but without success. The catalysts used were uranyl sulfate, mercuric oxide, copper sulfate, ferric and ferrous chloride, a compound catalyst consisting of equal parts by weight of the sulfates of ferrous ion, ferric ion, magnesium, manganous ion, and copper, and also without any catalyst at all. The results were entirely negative, except that traces of nitrites and nitrates were formed in the respective cases of mercuric oxide and ferric ion, and that uranyl formate decomposed to give uranium oxide and carbon dioxide, a reaction noticed previously by Schiller.[1] The ammonium ion was not oxidized by the uranyl sulfate. The reaction went rapidly to completion, .1 gm being decomposed by a 12-inch water lens in a few minutes. To illustrate the power of the condensed light used, it may be mentioned that a freshly prepared solution of ammonium carbonate and uranyl sulfate can be exposed to very bright sunlight for 15 minutes with scarcely perceptible change in color, but upon placing the same tube in the path of a beam of condensed light, a marked reaction is noticed in no more than a second, and in less than a minute the whole solution is entirely black or dark gray, filled with precipitated uranium oxide. During the first five seconds, the formation of intermediate oxides, indicated by a purple pink color, can be noticed.

The active concentration of carbon dioxide in the plant during the photoreduction process is, like the active concentration of light, not known, within fairly wide limits even, nor is its form (i.e. CO_2, HCO_3', CO_3'', etc.). For the present, it would not be unreasonable to suppose that the concentration, calculated as a gas might be, say, 10 atmospheres, which, expressed as carbonate would be about .5 M. Experiments were designed therefore, to obtain very much higher concentrations than have been used hitherto in similar experiments. This was accomplished by adding to ammonium carbonate various amounts of concentrated C.P. 35.0 N sulfuric acid. The acid was contained in a side arm sealed into the neck of the tube, and was not mixed with the rest of the contents in the bulb part until after vacuum sealing and until just a few minutes previous to exposure. .18 cc. of the acid neutralized .500 gms. of ammonium carbonate to full methyl orange, pH 3.0. The amounts of acid used varied from none at all to complete neutralization where as high as 10 atmospheres of gaseous carbonic acid were obtained. This arrangement allowed each form CO_2, HCO_3', and CO_3'' to predominate separately. The following catalysts were used: ferrous sulfate; ferric chloride; ferrous sulfate and ferric chloride; a mixture of equal parts by weight of manganous sulfate, nickel sulfate, copper sulfate, cobalt sulfate, chromic sulfate, ferrous sulfate, and ferric chloride; nickel sulfate; chromic and cobaltous sulfate; white zinc oxide; manganous chloride; manganous sulfate; malachite green (50 p.p.m.); uranyl sulfate.

Each exposed solution was examined by some thirty different tests. Not the slightest trace of detectable organic matter, nitrogenous or otherwise,

[1] Z. physik. Chem., **80**, 641 (1912).

was formed photochemically from the ammonium carbonate. Special attention may be called to the ineffectiveness of uranyl sulfate as a catalyst. There is reason to believe that if any carbonaceous substance had been formed, its transient existence would have been indicated by an irreversible photochemical reduction of the uranyl compound. The experiments of Usher and Priestley [1] in which formic acid was formed in some such system as was used here seem to be quite contradicted by these experiments, as well as by those of Baur and Rebmann.[2]

The only photochemical reaction observed was the oxidation of ammonia to nitrite or nitrate in the presence of ferric ion, the mixed catalyst and zinc oxide. The amounts found in the cases of the first two catalysts were the same and hence it may be assumed that the other substances in the catalyst neither promoted nor prevented the formation of nitrates especially since no nitrates were formed when each of the other substances was tried separately by itself. Zinc oxide was the most vigorous photocatalytic oxidizer of ammonia discovered some hundreds of parts per million of nitrate being produced upon a day's exposure in the presence of 2% ammonium chloride or carbonate. Presumably the active wave lengths are 350 to 400 $\mu\mu$, which are absorbed by the white zinc oxide. Solid zinc oxide phosphoresces in the ultra violet and if exposed beforehand to sunlight will cause the oxidation when added in the dark to aqueous ammonium salts. Exposed solid zinc oxide when added in the dark to the Griess reagent will give the nitrite test but not when similarly added to the Trommsdorff reagent, the reason being that the former contains nitrogen-hydrogen compounds while the latter contains no nitrogen compounds at all. The reaction was observed with either carbonate, chloride, or sulfate of ammonia. The rate depended directly upon the ammonium ion concentration and the surface of zinc oxide exposed, and did not seem to be affected by accumulation of end-products. There was no dark reaction over a considerable period of time if the zinc oxide had been kept away from the light previously. Neither clear saturated solutions of zinc oxide nor solutions of zinc salts, the chloride or the sulfate, possessed any catalytic activity, providing that all particles of solid zinc oxide were excluded.

The experiments with malachite green were extended considerably, and the results are detailed elsewhere.[3] Suffice to say that solutions of malachite green in the absence of any other substance were observed to decompose in sunlight to yield formaldehyde, amines, and under aerobic alkaline conditions, nitrites, in no case in concentrations greater than 10 p.p.m. Since the concentration of nitrite was only 1 p.p.m., there was no way of determining if nitrates were produced also. The nitrites were formed presumably from the nitrogenous decomposition products of malachite green, amines as well as ammonia.

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[1] Proc. Roy. Soc., **78B**, 318 (1906).
[2] Chim. Acta. Helv., **5**, 828 (1922).
[3] J. Am. Chem. Soc., in press.

Fenton's observation[1] that metallic magnesium may react with carbonates to give formaldehyde was confirmed. It was found also, that the amounts formed were not affected by the presence of either sunlight or ferric chloride.

Although the experiments of Moore and Dhar and Sanyal on synthesis are unconvincing, they have attracted wide attention nevertheless. The extensive experiments of the writer, in which more detailed analyses were made, are directly contrary to the results of these workers, and throw doubt upon the sufficiency of their technique. It is true that since ammonium sulfate, in addition to carbonic acid, was present in the writer's experiments, the experimental conditions were not exactly comparable; but so far as can be anticipated, this substance should have no critically harmful influence; quite the contrary, if formaldehyde and oxygen gas were the photochemical end-products of the reaction, the ammonia might assist in removing both of them, by forming hexamethylenetetramine (or other bases) and nitrites and nitrates. The negative character of the writer's experiments are upheld further by the fact that the C. P. chemicals used must have contained traces of many catalytic substances not introduced purposely.

The Oxidation of Ammonia by Ferric Chloride.

By way of positive results of interest particularly for the understanding of plant processes is the photochemical oxidation of ammonia by ferric chloride, one nitrate and eight ferrous ions being formed stoichiometrically. Nitrites can never be detected even after sunlight has been excluded from the exposed chamber for some time. In examining exposed solutions, the iron was removed by filtration after bringing the pH to 7. The following results with the filtered solution prove the formation of nitrates. The diphenylamine reaction was given, and only by those solutions exposed previously, but not by the controls. The latter fact alone precludes the possibility of traces of ferric ion being the causal agent, even though only 10 p.p.m. would be sufficient. At pH 7 an infinitesimal amount of iron can exist in solutions free from organic matter, and furthermore no tests with the three iron reagents previously mentioned were given. The fact that the Griess and Trommsdorff reactions were negative precludes, to a concentration of .1 ppm., nitrites, chlorine, chlorates, and hydrogen peroxide. Hydroxylamine has no effect on the diphenylamine reagent, and furthermore there was no reduction of N/200 permanganate, even though hydroxylamine reduces permanganate instantly in the cold. The fact that the reaction is given only when ammonia has been present, together with the observed stoichiometric relation (the ferrous ion was determined quantitatively with N/200 permanganate and qualitatively with ferricyanide) is good inferential evidence. The conclusive proof, however, is given by the fact that when powdered zinc is added, either when testing reagents are present at the same time or afterward, nitrites are formed in less than a minute in the cold, as shown by the Griess reaction, which is entirely specific for nitrites, and also by the Trommsdorff reaction, which, while not entirely specific for nitrites, is not given by nitrates. The zinc does

[2] J. Chem. Soc., **91**, 687 (1907).

not affect the Griess reagent, even upon long standing, and while it affects slowly the Trommsdorff reagent, advantage may be taken of the relative rates. Incidentally, this excellent but little known method of proving by reduction with zinc dust in the cold the specific presence of nitrates, in either the total or relative absence of nitrites, should prove welcome to analysts. The writer has seen no mention of it in the literature or in the standard analytical works.

The extensive proof above is given to avoid the usual criticism which can be made so justly of many physiological papers in which a single line of evidence for the existence of nitrates (usually the diphenylamine or phenoldisulphonic acid reaction) is considered sufficient.

The amounts of nitrate formed may reach as high as one hundred parts per million, and depend upon the concentration, pH, and intensity of light (as shown by using simultaneously different sized lenses and also by comparing with ordinary sunlight), but there is no direct proportionality with any of these factors. A stationary state, the cause of which is not yet understood, is reached, under any given set of conditions, after about a day's exposure. The half way point to this state is reached in less than an hour of bright sunlight. The reaction is unaffected one way or the other by the presence of oxygen gas. The back reaction of oxidation of ferrous ion in the dark, in either the presence or absence of air, is very slow, not greater, relatively, than one hundredth or more, nitrites being produced.

Bonazzi[1] believes that hydrogen peroxide is probably involved in the mechanism of nitrification by bacteria, where it is known that iron is essential for the process. No hydrogen peroxide (i.e., less than .1 p.p.m.) was observed in the writer's experiments.

The question of whether nitrates or nitrites are produced by any of the observed catalysts is interesting from a theoretical viewpoint, but probably the relations would be changed if the systems involved were not so homogeneous, and thus from the plant viewpoint, it is probably satisfying to know only that either is produced. In practically every photochemical experiment of the writer's where ammonium ion and ferric ion existed together, nitrates (but not nitrites) were found, indicating that the reaction may be of very general occurrence. The oxidation of ammonia to nitrite or nitrate at ordinary temperatures in the dark is accomplished with difficulty by even the strongest oxidizing agents, such as concentrated permanganate, chromate, etc., and hence the importance of the photochemical reaction is established. According to Baudisch and Baly the photochemical elaboration of nitrogen compounds may proceed from the nitrite stage and go through the formhydroxamic acid stage. The end-products of synthesis in plants are protein like bodies in which the nitrogen is in an ammonia-like form (i.e., NH, NH_2, NH_3). The question would arise then, when plants are nourished with ammonium salts, must these be oxidized to nitrites, then be reduced to formhydroxamic acid, and then proceed to an ammonia form? There is no reason

[1] J. Bact., 8, 343 (1923).

why a plant should make use of what seems to be the most direct path, and the writer believes that his work, in combination with that of Baudisch and Baly, shows that such an indirect path in plants is possible, and furthermore, may proceed without loss of efficiency, which could occur, for instance, by the formation and loss of nitrogen gas, as an intermediate product. It is true that Baly has another suggestion[1] for taking care of the synthesis from ammonia, by means of the activated formaldehyde postulation. Since this discussion applies chiefly to what *may* occur in plants, it is not difficult to imagine other quite possible paths; and furthermore it is well known that the elaboration of proteins in plants can take place in the dark. However, if elaboration is photochemical, the probability of the indirect path suggested above is strengthened further by the unsuccessful attempts of the writer in trying to accomplish synthesis by the direct path.

In speculative vein, it may be suggested that nitrification in soils may be accomplished on the surface by means of sunlight and photocatalysts. There are reasons to believe, that in addition to the catalysts observed, many oxides, particularly those which absorb the sun's ultra violet light, could function also as catalysts, becoming reoxidized by the air. Conceivably the "nitre spots" in Colorado, reported by Headden and Sackett[2] in a series of papers since 1910, are formed for the reason, in part, that the soil contains some very efficient photochemical nitrifying catalyst which is able to oxidize quickly the ammonia fixed by the nitrogen fixing bacteria. It should be remembered that the formation of nitre spots always requires fairly moist conditions, just as the photochemical reaction presumably would. The severe criticism to be made of the biological explanation as being entirely sufficient for the accumulation of nitrates, is that the concentrations of nitrate formed (as great as 5% of the bulk of the soil) should preclude the action of organisms in the later stages. The suggested photochemical mechanism of nitrification would not be open to this objection, however, if the writer's experiments with zinc oxide may be used as an indication. The accumulated nitrate had no noticeable effect on the amount formed; nor could it be expected to have, *a priori*, in the sense that the reaction, being photochemical, is hardly subject, according to present views, to the mass law.

Summary

Some five hundred photosynthesis experiments with systems involving ammonia and various carbonaceous substances, including carbon dioxide, formic acid, formaldehyde, and glucose, were performed. Sunlight condensed through twelve-inch lenses, in combination with colored inorganic catalysts, was used, the exposures being made in very thin glass vessels.

Only one type of photochemical change with ammonia was observed; in the presence of ferric chloride, ammonia was oxidized to nitrates; in the presence of zinc oxide and mercuric oxide to nitrites and nitrates. Hydroxylamine was never produced.

[1] Rice Inst. Pamphlet, **12**, No. 1, p. 85.

[2] Col. Exp. Sta. Bull., **155, 178, 179, 186, 193, 239, 258, 299, 277, 291.**

No photochemical reduction of carbonic acid was observed.

No complex biochemical nitrogen compounds were produced from ammonia and carbonaceous substances.

It is felt that owing to the enormous range of concentrations of sunlight used, number of experiments performed, variety of conditions maintained, carefulness of technique employed, involving the necessary precautions to avoid contamination by organic matter, and the extensiveness of the methods of analysis, considerable doubt has been thrown upon the positive photosynthesis results of Moore, Dhar and Sanyal, and others, who have employed sunlight and inorganic catalysts also.

The writer wishes to express appreciation of the advice and assistance given by Professor Dennis R. Hoagland and Professor Charles W. Porter throughout the course of this investigation.

Division of Plant Nutrition and Department of Chemistry,
University of California, Berkeley.

SOCIÉTÉ DE CHIMIE INDUSTRIELLE
28, Rue St-Dominique
ANNULÉ

THE THERMAL DECOMPOSITION OF HYDROGEN PEROXIDE[1]

BY F. O. RICE AND ORLAND M. REIFF[2]

The results of numerous investigations on the thermal decomposition of hydrogen peroxide indicate that the reaction takes place mainly in homogeneous solution and is only slightly catalysed by the walls of the reaction vessel. However practically all previous work deals not with pure aqueous solutions, but with solutions containing alkalies, salts, catalytic metals and preserving agents. In spite of the fact that hydrogen peroxide is a simple compound whose rate of decomposition can easily be measured, the values for the velocity constants, when calculated according to an unimolecular formula are characterised by large discrepancies although obtained under apparently identical conditions. For example, Clayton,[3] in an extremely careful study of the thermal decomposition of dilute aqueous solutions of hydrogen peroxide, concluded that the purity of the water is an important factor in the decomposition whereas Lemoine[4] concluded that the state of the surface of the containing vessel is the most important factor.

In this paper we present the results of an investigation in which we paid special attention to the following points; (1) we ensured the absence of traces of inhibitors by preparing our own hydrogen peroxide according to a method[5] already published; (2) we removed all colloidal matter and suspended dust particles as described[6] in a previous article; (3) before making a velocity determination we melted the surface of the vessel to remove the frittering of the surface of glass and quartz that occurs on standing. Our results indicate that the ordinary decomposition of hydrogen peroxide is due mainly to suspended dust particles but is also caused to some extent by the surface of the vessel; any homogeneous decomposition of hydrogen peroxide is negligibly slow compared to the heterogeneous decomposition.

The rate of decomposition of hydrogen peroxide was measured chiefly by the volume of gas evolved, but since this method is open to several criticisms the final results were always checked by experiments in which portions of the solution were withdrawn at measured time intervals, weighed and titrated with permanganate in the usual manner. The experiments were conducted usually in a Pyrex vessel surrounded by an outer jacket fitted with a reflux condenser so that the inner vessel could be kept at a given temperature by the vapor of a suitable liquid; usually the experiments were conducted at the temperature of boiling benzene.

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[1] Contribution from the Chemical Department of Johns Hopkins University.

[2] Abstracted from the thesis of Orland M. Reiff presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy of the Johns Hopkins University.

[3] Clayton: Trans. Faraday Soc., **11**, 164 (1915).

[4] Lemoine: J. Chim. phys., **12**, 1 (1914).

[5] Kilpatrick, Reiff and Rice: J. Am. Chem. Soc., **48**, 3019 (1926).

[6] Rice: J. Am. Chem. Soc., **48**, 2099 (1926).

In previous work but little attention has been given to the quality of the hydrogen peroxide used; ordinary commercial solutions contain various substances as impurities, most commonly phosphoric, sulfuric and hydrochloric acids; the most common preservatives are uric acid, barbituric acid, acetanilide and quinine sulfate. Even the very best brands of hydrogen peroxide which are guaranteed free from added inhibitor, usually are supplied in paraffin bottles so that there is the possibility that the paraffin may supply a minute

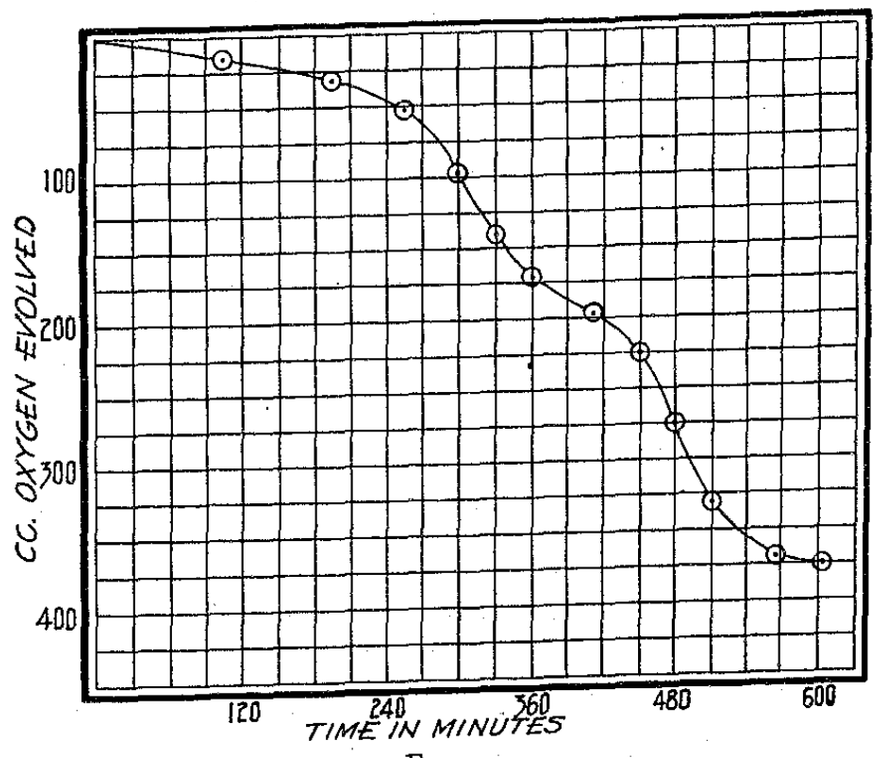


FIG. 1
Decomposition of Merck's Perhydrol, D.R.P. 216263, 0.674M hydrogen peroxide. Temp. 80.2°C.

trace of organic preservative either through an actual impurity in the paraffin or by slight oxidation by the hydrogen peroxide. In order to clear up the effect of inhibitors as far as possible we made a preliminary study of the rate of decomposition of various commercial products and also the rate of decomposition of our own pure hydrogen peroxide to which various inhibitors were added.

Fig. 1 gives the curve showing the decomposition of solutions of Merck's perhydrol. This curve is characterised by the occurrence of two induction periods. The type of curve was found to be the same regardless of the concentration; however the breaks in the curve are more pronounced in solutions of higher concentration. Exactly the same type of curve was obtained by either the gasometric or titration method, leaving beyond doubt the accuracy of the experimental procedure. It is interesting to note that Baker's analysed hydrogen peroxide and Merck's German product S. 7456, while giving an initial period of inhibition do not give the second inflexion in the curve.

Fig. 2, Curve 1, shows the type of curve obtained in the thermal decomposition of our own pure hydrogen peroxide to which was added any of

the following inhibitors: barbituric acid, uric acid, benzamide, acetanilde, tannic acid or quinine sulfate. In these experiments pure 30% hydrogen peroxide prepared by us was added to ordinary distilled water and then the desired amount of inhibitor added. These curves which were all similar, are characterised by an initial fast period followed by a single inhibition. Acetanilide and tannic acid were found to be the least active preservatives, being

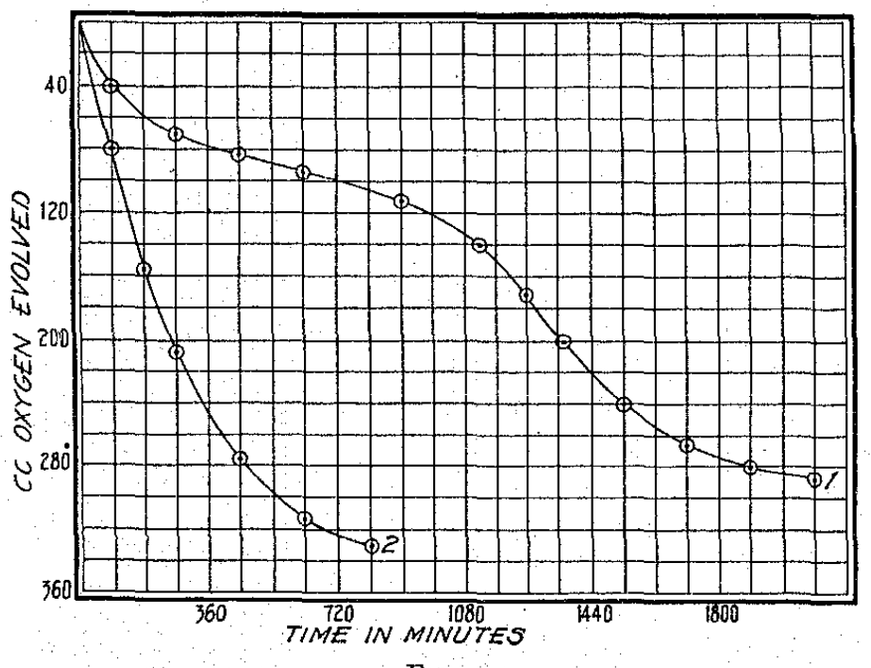


FIG. 2

Curve. 1. Decomposition of 0.6 M hydrogen peroxide containing 0.003% uric acid. Temperature 80.2°C.

Curve 2. Same solution restored to the original strength by addition of pure 70% hydrogen peroxide.

less than one third as effective as barbituric acid, benzamide and quinine sulfate. Fig. 2, Curve 2 was obtained in the following way; the rate measurement shown in Fig. 2, Curve 1, was made and then the experiment was repeated with the same solution restored to its original strength by the addition of the required amount of a 70% solution of pure hydrogen peroxide. This experiment was repeated with several other preservatives but in all cases there was complete absence of any inhibition indicating that during the course of any experiment the inhibitor is destroyed.

The thermal decomposition of pure aqueous solutions of hydrogen peroxide free from both organic and inorganic inhibitors appears not to have been previously investigated. Curve 2, Fig. 3, shows the decomposition of a solution of hydrogen peroxide, made by dilution of the pure concentrated product with water made from a silica still. The curve follows a straight line for practically the entire decomposition and represents the minimum velocity obtained with dusty but alkaline free solutions. If however tap water is used not only is the rate of decomposition faster but the curve is no longer a straight line but approximates the curve for an unimolecular decomposition (Fig. 3, Curve 1). The higher rate is due partly to the higher dust content

but chiefly to the alkalinity of the tap water. We have found that when the peroxide solutions contain impurities such as chlorides, alkaline substances, inhibitors, etc the curves obtained are never straight lines and often approximate curves for unimolecular decompositions.

Our next step was to reduce the dust content of the peroxide solution by the method described by Martin.[1] Unfortunately this method is not too well suited

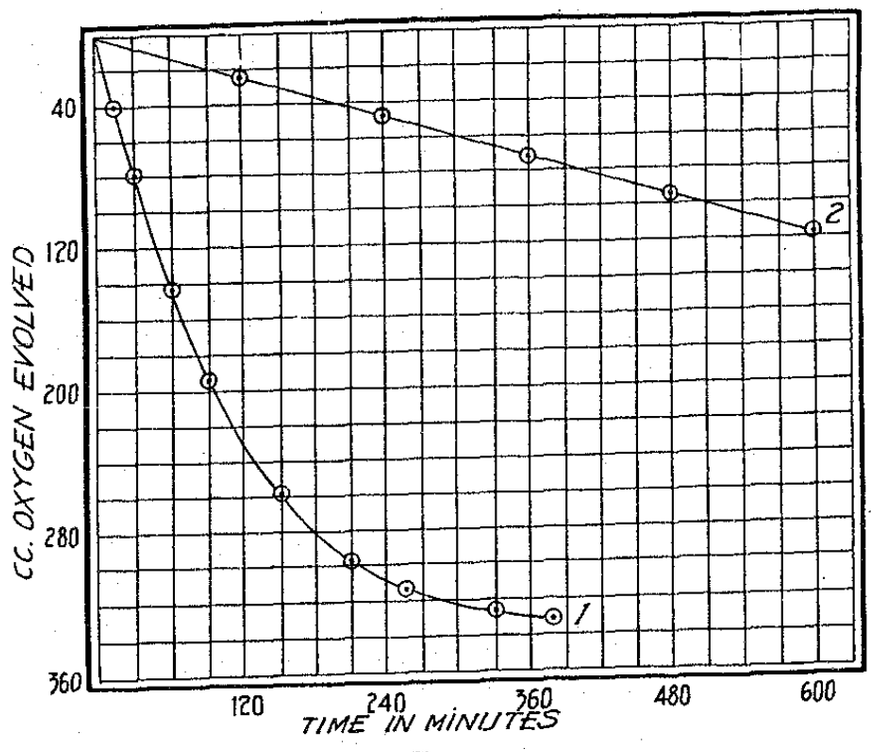


FIG. 3

Decomposition of 0.6 M hydrogen peroxide at 80.2°C.
Curve 1. Pure 70% hydrogen peroxide diluted with tap water.
Curve 2. Pure 70% hydrogen peroxide diluted with distilled water from a silica still.

for the removal of dust from peroxide solutions because the peroxide decomposes very slightly during distillation which causes ebullition to some extent; however we found that we could greatly diminish the dust content and by conducting experiments with this peroxide in a vessel of freshly fused silica we obtained very low rates of decomposition. In one experiment 45cc. of a 2% solution evolved oxygen at the rate of 3cc. per hour at 80°C. Our whole experience indicates that complete removal of dust and conducting the experiment in a vessel with smooth walls would lead to a negligibly small rate of decomposition.

We measured the rate of decomposition of a solution of hydrogen peroxide (free from inhibitors but containing dust) at 60° and 80° C and calculated for K_{80}/k_{70} the value 3. Lemoine found for his solutions a value between 2 and 3.

The absence of inhibition periods in the curves for the decomposition of pure solutions of hydrogen peroxide led us to investigate the reaction described by Bray and Caulkins[2] on the catalysis of hydrogen peroxide by the iodine-

[1] Martin: J. Phys. Chem., **24**, 478 (1920).
[2] Bray and Caulkins: J. Am. Chem. Soc., **43**, 1262 (1921).

iodic acid couple. We were able to obtain results approximately similar to those of Bray and Caulkins by using various commercial samples of hydrogen peroxide; the shape of the curve depends however very much on the regularity of stirring, the rate of evolution of oxygen being very sensitive to this factor.

The use of commercial solutions properly purified from inhibitors by distillation, or the use of our own pure hydrogen peroxide gave curves without a periodicity whereas the addition of inhibitors again caused the phenomenon of periodicity. It seems probable therefore that the decomposition of hydrogen peroxide by the iodine-iodic acid couple is also a heterogeneous reaction similar to the thermal decomposition of hydrogen peroxide; the experimental difficulties however prevented us from removing the dust from these solutions and subjecting the matter to a rigorous test.

Summary

1. The decomposition of hydrogen peroxide in the presence of preservatives is characterised by an initial period of inhibition after which the material decomposes at a rate somewhat similar to an unimolecular reaction.

2. When hydrogen peroxide is prepared free from traces of organic inhibitors, chlorides, etc., its decomposition is approximately a zero order reaction.

3. When solutions of hydrogen peroxide are prepared free from suspended matter and in vessels with smooth walls, the rate of decomposition is exceedingly slow. The ordinary decomposition of hydrogen peroxide takes place on the surface of dust particles and on the walls of the vessel and an inhibitor evidently acts by poisoning the surface.

4. The decomposition of hydrogen peroxide by the iodine-iodic acid couple also appears to be a heterogeneous reaction occurring on the surface of dust particles.

Baltimore, Md.

A STUDY OF PHOTOVOLTAIC CELLS

BY CARL W. TUCKER

Introduction

If a photosensitive substance is placed upon two metal electrodes which dip into some solution, the potential difference between these two electrodes, in the dark, may be brought to zero. But if one of these electrodes is illuminated while the other is darkened, the photochemical changes which take place on the illuminated surface, may be expected to produce a potential difference between the exposed and darkened electrodes. What the magnitude of this voltage will be and what will be the sign of the charge on the illuminated electrode, may be expected to vary with the nature of the photosensitive substance and its light-reaction.

Becquerel[1] was the first to prepare a light-sensitive cell of this type. The effect produced upon proper illumination of such a cell has since been termed the "Becquerel effect." The cell arrangement, as described is designated as a "photovoltaic cell."

Becquerel adopted silver chloride, bromide, and iodide as photosensitive substances, and these were placed upon electrodes of silver or platinum. The cell solution used was a dilute sulfuric acid. He observed, from the beginning, that the sign of the charge on the illuminated electrode varied with the thickness of the photosensitive material on the metal surface. He also pointed out that the observed voltage was inconstant during the illumination and that its value varied with the intensity of the illumination.

From Becquerel's experiments, we may draw the following conclusions:

(Throughout this paper, that electrode from which current flows in the cell solution, is considered as being negatively charged, and is called an anode, *i. e.* as zinc in a copper-zinc cell. An arrow included in the cell diagram designates the direction of current flow in the cell solution.)

1. The photosensitive silver halides, placed on platinum sheet and made up into a photovoltaic cell with dilute sulfuric acid, form an electrode which functions as a cathode in the cell under proper illumination.

2. The photosensitive silver halides, placed on silver sheet and made up into a photovoltaic cell with a solution containing a small amount of sulfuric acid, all form photosensitive electrodes which vary in their electrical behaviour, as the silver halide thickness or uniformity on the electrode surfaces is varied. With a thin layer of the halides on the silver electrode, it becomes a cathode upon illumination and with a thicker or more uniform layer, it functions as an anode upon illumination.

In 1891, Minchin[2] recorded his observations on photovoltaic cells made up from several different electrode metals and using varied cell solutions. Min-

[1] La Lumière, II, 121.

[2] Phil. Mag., (5) 31, 207 (1891).

chin's results again impress one with the indefiniteness of the electrical effects observed. In some cells the illuminated electrode was found to be an anode. In others the reverse effect was observed. In still other cells both effects were found. Indeed, in regard to this latter point, I wish to quote Minchin exactly:

"In nearly every cell that I used with tin plates—whose surfaces, as stated above, had not been treated in any way—the exposed plate was positive to the unexposed; but after a time varying from a few minutes to a few hours, it was found that this positive current died out and was replaced by an apparently stronger current, in which the exposed electrode was negative. Thus there was a change in the sign of the E. M. F. produced by the continuous action of light. This again reminds us of M. Becquerel's observation about the thickness of sensitive layers. There seemed to be almost no exception to the rule that the exposed electrode begins by being positive and ends by being negative, the negative regime lasting for many days of prolonged exposure to light."

I should point out that Minchin called the positive plate or electrode, the plate from which current flowed in the cell. That is, his nomenclature is the reverse of the one that I have adopted.

Among the first photosensitive materials that Minchin used, again, were the three silver halides placed on metallic silver. Minchin prepared these sensitive electrodes by making a collodion emulsion of the silver halide which was then allowed to harden as a film on the silver plate. His cell solutions were different from those of Becquerel; sodium chloride, sodium bromide, and silver nitrate solutions being used with the silver chloride, silver bromide, and silver iodide coated electrodes, respectively.

The results which Minchin found upon individual illumination of these three photovoltaic cells, are different from those recorded by Becquerel. With the cell arranged as follows:

$$\text{Illuminated Ag} \mid \text{AgCl} \qquad \underset{\longleftarrow}{\text{NaCl}} \qquad \text{AgCl} \mid \text{Ag}$$

the exposed electrode was found to be a cathode.

In the cell,

$$\text{Illuminated Ag} \mid \text{AgBr} \qquad \underset{\longleftarrow}{\text{KBr}} \qquad \text{AgBr} \mid \text{Ag}$$

the illuminated electrode was again found to be a cathode. But in the cell,

$$\text{Illuminated Ag} \mid \text{AgI} \qquad \underset{\longrightarrow}{\text{AgNO}_3} \qquad \text{AgI} \mid \text{Ag}$$

the exposed electrode was found to be an anode.

Minchin devotes the remainder of his paper to a record of results observed with photovoltaic cells made up of different metals in various solutions. Since many of his conditions are not sufficiently described in detail, it is difficult to interpret all of his results. We may at least note in his work the following points:

1. Illumination of a metal surface which has some photosensitive substance present, either as a film or in denser masses, will produce a photovoltaic effect.

2. The nature of the photochemical changes taking place at an electrode surface is recorded indirectly by the direction of flow of the current produced in the photovoltaic cell.

3. This direction of current flow is found to vary with the nature of the cell solution, the photosensitive substance, the electrode metal, and the thickness of the photosensitive substance as an electrode surface layer. Hence we conclude that the nature of the photochemical actions must vary with each of these variables.

4. Minchin's record of the fact that in many cells he found an initial effect in which the current flowed in one direction in the cell, and then reversed as illumination continued, indicates that a change in the various possible photochemical or electrochemical actions at the illuminated electrode face, must occur, during the period that the cell is being illuminated.

Wildermann[1] studied very carefully some photovoltaic cells of the simpler type. By a photographic method, he succeeded in constructing an accurate representation of the relation between galvanometer deflections and time of illumination. He did not study any of those cells types in which the photosensitive substance is present as a thick or uniform layer on the electrode surfaces.

Wildermann found that the illuminated electrode was a cathode in all of the following systems:

Illuminated	Ag | AgCl (Thin layer)	0.1N NaCl ←	AgCl | Ag (Thin layer)
"	Ag | AgBr (Thin layer)	0.1N NaBr ←	AgBr | Ag (Thin layer)
"	Ag | AgBr (Thin layer)	0.1N KBr ←	AgBr | Ag (Thin layer)
"	Ag | AgBr (Thin layer)	0.1N LiBr ←	AgBr | Ag (Thin layer)
"	Ag | AgI (Thin layer)	0.1N KI ←	AgI | Ag (Thin layer)
"	Hg | Hg_2SO_4 (Thin layer)	0.1N K_2SO_4 ←	Hg_2SO_4 | Hg (Thin layer)
"	Cu | CuO (Thin layer)	1/40N NaOH ←	CuO | Cu (Thin layer)

[1] Wildermann: Z. physik. Chem., **59**, 553, 703 (1907).

From Wildermann's time-volt curves we can deduce that the photovoltage slowly approaches a maximum and falls quite rapidly to the original potential difference between the unilluminated electrodes, as the source of light is removed.

Case[1] produced a photovoltaic cell with electrodes consisting of a uniform layer of cuprous oxide on metallic copper. The illuminated electrode in this cell was an anode when the cell solution contained about 2.5% copper formate and 0.4% formic acid. The new observation which Case made, was the behavior of this particular cell when illuminated with the external circuit closed. It was found that, if one electrode was illuminated and the other kept dark, a current was produced which flowed in the cell solution away from the illuminated plate and developed initially an E.M.F. of 0.11 volts. Upon continued illumination with the external circuit closed through a current measuring instrument, the current finally dropped to zero; but if the cell was now rotated, illuminating the previously darkened plate, the E.M.F. reappeared, current again flowing away from the exposed electrode. This action could be continued indefinitely. Case further stated that if these same electrodes with their photovoltaic coating, were transferred to a dilute sodium chloride solution and one electrode illuminated, the exposed electrode became a cathode.

We may draw these conclusions from this paper by Case:

1. A uniform layer of cuprous oxide on copper in a proper solution, behaves electrically in the same manner as did Becquerel's uniform layer of silver chloride on silver in a dilute sulfuric acid solution.

2. A uniform layer of cuprous oxide on copper, illuminated in a sodium chloride solution as a cell electrode, behaves in the same manner as did Minchin's uniform layer of silver on silver chloride in a dilute sodium chloride solution.

3. Upon continued illumination of Case's photovoltaic cell with the external circuit closed, the photosensitive material upon the copper electrode surface seems to be destroyed. Simultaneously, it is reformed on the darkened electrode.

Cuprous oxide-copper photovoltaic cell electrodes were carefully studied for the first time as regards density and uniformity of the cuprous oxide film, and the effect of a variation in the cell solutions used, by Garrison.[2] He devised a method of placing a layer of cuprous oxide on copper by which the density of the layer could be readily varied, as desired. His method consisted in dipping a polished copper sheet into a cupric formate solution and hydrolyzing the cuprous formate formed on the copper surface. Each time this procedure was repeated, the density and uniformity of the oxide layer was increased. Garrison records a point which is of interest as viewed in the light of the preceding researches. He found that many cuprous oxide-copper electrodes gave an initial anode tendency when illuminated, but upon continuous

[1] Case: Trans. Am. Electrochem. Soc., **31**, 351 (1917).
[2] Garrison: J. Phys. Chem., **27**, 601 (1923).

illumination this effect reversed. The initial anode effect was found to increase and the reverse cathode effect to decrease, as the density and uniformity of the cuprous oxide layer on the copper electrode surfaces was increased. Garrison in this respect substantiated the reversal rule first pointed out by Minchin.

This paper by Garrison may be summarized as follows:

In the cell type,

Illuminated	$Cu \mid Cu_2O$ (Thin layer)	K_2SO_4 $\longleftarrow$	$Cu_2O \mid Cu$ (Thin layer)

the illuminated electrode is a cathode. If this cell is illuminated with a closed external circuit, a current reversal takes place when the light-source is removed. If a potentiometer is used to observe the photovoltage, no current being allowed to pass through the cell as measurements are being made, this reversal tendency does not exist.

In the cell type,

Illuminated	$Cu \mid Cu_2O$ (Dense layer)	K_2SO_4 $\longrightarrow$	$Cu_2O \mid Cu$ (Dense layer)

the illuminated electrode is an anode.

In a cell of the type,

Illuminated	$Cu \mid Cu_2O$ (Medium density)	K_2SO_4	$Cu_2O \mid Cu$ (Medium density

in which current tends to flow from the illuminated electrode in the cell, addition of sulfuric acid to the cell solution reverses the anode tendency. Addition of potassium hydroxide increases the original anode tendency. When solid copper sulfate is added to the potassium sulfate cell solution the original tendency of current flow from the illuminated electrode is diminished. On the other hand, addition of copper sulfate to a cell of the type,

Illuminated	$Cu \mid Cu_2O$ (Thin layer)	K_2SO_4 $\longleftarrow$	$Cu_2O \mid Cu$ (Thin layer)

in which the illuminated electrode is originally cathode, causes a reversal and an anode effect becomes apparent.

In all of the above types in which current reversal tends to take place as the nature of the cell solutions are varied, the Minchin reversal phenomena always becomes prominent at the time the change in direction of current flow takes place.

Using the same method of attack, Garrison[1] made a study of the photovoltaic cell,

Illuminated	Ag | AgI	Solution	AgI | Ag

[1] J. Phys. Chem., **28**, 333 (1924).

in which he varied again the density of the halide layer on the silver surface, as well as the cell solution. It was again found that the illuminated electrode was cathode in

Illuminated	Ag | AgI (Thin layer)	K_2SO_4 ←	AgI | Ag (Thin layer)

By coating the silver with the silver iodide through an electrochemical method, Garrison found that the illuminated electrode became an anode when the density and uniformity of the silver halide layer was increased.

Illuminated	Ag | AgI (Dense layer)	K_2SO_4 →	AgI | Ag (Dense layer)

He also again found, that with continued illumination of the above cell, the original anode tendency of the exposed electrode was reversed. He found that addition of silver nitrate to the potassium sulfate solution increased the original anode tendency, while additon of potassium iodide increased the cathode tendency of the illuminated electrode.

We may conclude from Garrison's papers, that the diverse observations recorded in the extant literature, regarding photovoltaic cells in general, may be eventually explained by a proper study of the density and uniformity of the photosensitive layer and the effect of the cell solution, since even slight variations in these two factors change the behaviour of the cells under illumination.

EXPERIMENTAL STUDY

Introduction

This paper attempts to explain the behaviour of illuminated photovoltaic cells, through a discussion and experimental study of the cuprous oxide and silver halide photovoltaic systems. The viewpoints which will be introduced may be summarized as follows:

1. Both the nature of the cell solution and the nature of the metal with which the photosensitive material is in contact will be factors in determining the photochemical reactions which take place under illumination.

2. Local cells may form on the surfaces of the illuminated electrode. These can have a marked effect upon the nature of the potential difference found to exist between the two massive electrodes of the photovoltaic cell proper.

3. In the case of a thick or uniform layer of the light-sensitive substance on an illuminated metal sheet, these local cells will be at a minimum. They will be at a maximum in the case of thin or non-uniform layers of the photosensitive substance on an illuminated metal sheet.

4. The solutions used in the photovoltaic cell may be varied in such a way as to throw these local cells into the reversible or irreversible types of cells. The behaviour of the photovoltaic cell under illumination will accordingly be found to vary as the cell solution is varied.

Apparatus

In order to simplify the cell behavior as much as possible, the photovoltage obtained upon illumination was always determined by a potentiometric method. Since practically no current passes through the cell when this method is used, the occurrence of a secondary electrode polarization is prevented.

The cell electrodes used were of two types, the sheet electrode and the wire gauze electrode. The sheet electrodes were made from a thin rolled sheet, 8×3 cm. A copper wire connection was attached by soldering, in the case of the copper electrodes and by wrapping the wire into the thin sheet, in the case of the silver electrodes. In use, about a 6 cm. length of the electrode was immersed in the cell solution. Except in a few cases, the electrodes were not coated with an insulator of any kind on their back and unilluminated surface. The gauze electrodes were slightly larger than the sheet, having dimensions of about 6×6 cm. and a gauze wire diameter of .5 mm. with a gauze size of 40 mesh/inch.

The photovoltaic cell vessel consisted of an ordinary, glass, flat-walled, absorption cell, $4 \times 10 \times 10$ cm. The exposed electrode was shielded from the illuminated electrode by a piece of black sheet rubber dropped down between the two electrodes. A Leeds and Northrup student potentiometer in connection with a Leeds and Northrup reflecting galvanometer sensitive to 82.2 megohms, was used for measuring the photovoltages. The source of light was a 200-watt bulb on a 110 A.C. line, placed at a distance of 10 cm. from the electrode face, with no reflector. In practice, electrodes were always made in duplicate, and by a system of two 200-watt bulbs, each cell electrode could be individually illuminated and observed, the one serving as a check on the behaviour of the other. Since in many cases, important reversals in the photovoltage occur during the period of illumination, the ordinary tap-key was not considered sufficiently rapid, as a galvanometer connection. For this reason, a switch was arranged so that the galvanometer could be permanently connected to the cell during the 10 to 15 second illumination periods. The photovoltaic current was at the same time accurately balanced by changing the potentiometer slide-wire adjustment in such a way that the galvanometer showed zero deflection at all times. By this method, variations in the directional tendency of the cell current were accurately registered in the varying settings of the potentiometer.

The Cuprous Oxide-Platinum Photovoltaic Cells

Bancroft[1] has pointed out that the nature of a photochemical action can be determined by the chemical environment of the illuminated system. A photosensitive substance may be expected to be photochemically oxidized when illuminated in an oxidizing environment. A photosensitive substance may be expected to be photochemically reduced when illuminated in a reducing environment. Cuprous oxide, as a photosensitive substance, would be expected to possess the possibility of undergoing either photochemical oxidation

[1] J. Phys. Chem., **12**, 209 (1908).

to cupric oxide or a photochemical reduction to copper. If we place cuprous oxide on platinum, as an inert metal, and make it an electrode in a photovoltaic cell in which both oxidizing and reducing solutions are used, we should be able to obtain a confirmation of these ideas, as indicated by a variation in the cell behaviour as various solutions are used.

Consider the photovoltaic cell,

$$\text{Illuminated Pt} \mid Cu_2O \qquad \text{Reducing Solution} \qquad Cu_2O \mid \text{Pt}$$

in which one electrode is illuminated. Photochemical reduction of the cuprous oxide will tend to take place at the surface of the exposed electrode. A potentiometer applied to the cell terminals should show that the two electrodes are not in equilibrium, and that the exposed electrode is tending to function as an anode, in order to restore the equilibrium through an oxidation of reduced cuprous oxide and a reduction of cuprous oxide at the darkening electrode.

Similarly, if we have the cell,

$$\text{Illuminated Pt} \mid Cu_2O \qquad \text{Oxidizing solution} \qquad Cu_2O \mid \text{Pt}$$

illumination of one electrode will produce a photochemical oxidation of the cuprous oxide on the platinum. The cell now being out of equilibrium, a potentiometer will show that a current is tending to flow in a way that will make the illuminated electrode a cathode. Equilibrium is tending to be restored through a reduction of oxidized cuprous oxide at the illuminated surface and an oxidation of cuprous oxide at the unexposed electrode surface.

In such a cell with a neutral solution, the presence of dissolved atmospheric oxygen in the solution may possibly supply enough of an oxidation potential to cause the illuminated electrode to appear as a cathode.

These various cell types were set up and their behaviour observed. It is difficult to place cuprous oxide on a platinum surface in such a way that it will adhere when the electrode is dipped into a solution. This problem was solved by making precipitated and washed cuprous oxide into a thick paste with a little water, and rubbing it upon the face of a platinum gauze electrode. The cuprous oxide penetrated into the interstices of the gauze, and was found to remain satisfactorily in that location, even when the electrode was dipped into a cell solution. All of these platinum-cuprous oxide electrodes were prepared in this fashion. The cuprous oxide was made by precipitation from hot Fehling's solution with glucose and washing the precipitate well with hot water.

The results obtained with these electrodes illuminated in various solutions, are indicated in the curves shown in Fig. 1. In these curves the ordinates represent anode or cathode behaviour of the illuminated electrode and total voltage difference between the two cell electrodes. The abscissas correspond very roughly to time of illumination in seconds. These curves are not to be considered as a quantitative representation of behaviour, but rather, as a convenient method of illustrating qualitative results. They have all been drawn free-hand, after the cell had been set up and illuminated.

In none of these cells was a maximum voltage obtained in the time of illumination. The cell was only illuminated for a period of 10 to 15 seconds, since the thermal effects began to become appreciable after that time.

The cell solutions used were 0.1 N except in the case of the acidified potassium sulfate and the potassium hydroxide and potassium sulfate mixtures. In these the acid or alkali were added in solution and dropwise until a definite indication of acidity or alkalinity was shown by litmus paper.

In order to ensure that these observed effects were produced by the photosensitive cuprous oxide alone, the platinum gauze, free from any oxide, was illuminated in all of the solutions used. Either no effect or negligible effects

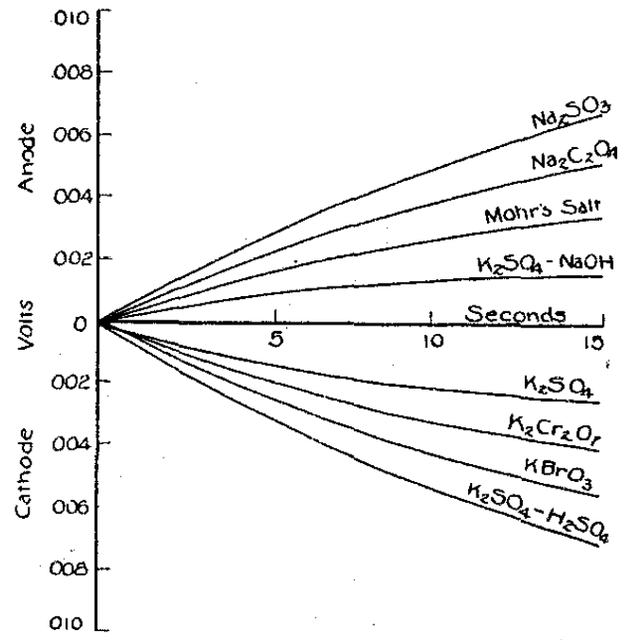


FIG. 1
Behaviour of platinum-cuprous oxide electrodes illuminated in oxidizing and reducing solutions.

were found. The photovoltages observed with cuprous oxide on platinum were small but definite. They indicate that in all reducing solutions, photochemical reduction of cuprous oxide tends to take place; and in all oxidizing solutions, photochemical oxidation of cuprous oxide tends to take place.

The Cuprous Oxide-Copper Photovoltaic Cells

In order to determine whether or not the electrode metal has its own specific effect on the action of the photovoltaic cell, it would be desirable to repeat the above experiments, with the one substitution of a copper gauze electrode. Any variations in behaviour can then be attributed at once to the difference between the metals, copper and platinum.

Before making the experiments, we can point out another possible variation in the cell behaviour, which may be expected.

If we consider again, the platinum gauze electrode containing cuprous oxide in its surface, and if we agree that the photovoltaic behaviour of this electrode is produced by the illuminated cuprous oxide, a complicating factor enters.

In electrodes of the gauze type, the back of the illuminated electrode is darkened but is intimately connected electrically, by the metal and the conducting solution, with the front and illuminated surface. Hence, we should expect a series of local cells to be set up on the face of the illuminated electrode, in which current will flow between illuminated and unilluminated points of cuprous oxide on platinum, or even between points of illuminated cuprous oxide on platinum and illuminated platinum. As pointed out, the possibility of this current flow in local cells is greatly increased by the peculiar construction of the gauze electrode, as compared with a sheet electrode. It follows also, that the potential difference between the illuminated and unilluminated massive electrodes of the photovoltaic cell proper, is determined only as a secondary thing and after the equilibrium adjustment is attained among the local cells on the illuminated gauze electrode surface.

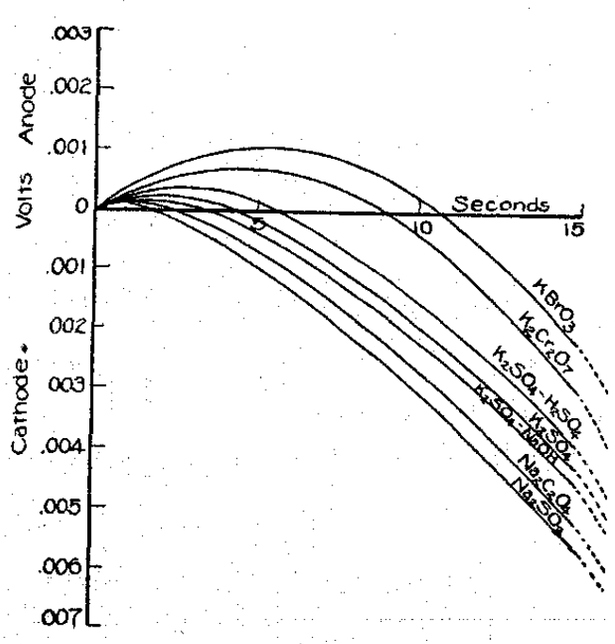


FIG. 2
Behaviour of copper gauze-cuprous oxide electrodes illuminated in oxidizing and reducing solutions.

In the case of cuprous oxide on platinum, the effect of these local cells will be negligible, since the inert platinum cathode and anode in the local cell tends to polarize at once if any current passes through the system.

If, on the other hand, the platinum gauze is replaced by a copper gauze, this polarization may not occur. Since copper electrodes are not inert, the metal anodes of these local cells will tend to pass into solution. These ions passing into solution about the illuminated electrode surface, at once increase the possibility of many new variations in electrode behaviour. But in every case, the photovoltage which we can determine between the illuminated and unilluminated massive electrodes will be determined only after the local cells have reached an equilibrium or attempt to reach equilibrium.

The results of experiments using copper gauze electrodes, pasted with cuprous oxide, in various cell solutions, are shown in Fig. 2. In this case, the

clean copper gauze free of oxide was previously illuminated in each of these solutions and found not to be photosensitive. The results obtained can be attributed to the original photosensitivity of cuprous oxide.

We may summarize these results as follows:

1. The presence of copper metal in the electrode has a specific effect on the behaviour of the copper-cuprous oxide cell.

2. These cells with copper gauze electrodes show the so-called "Minchin effect." The illuminated electrode is anode at first, then becomes cathode upon continued illumination.

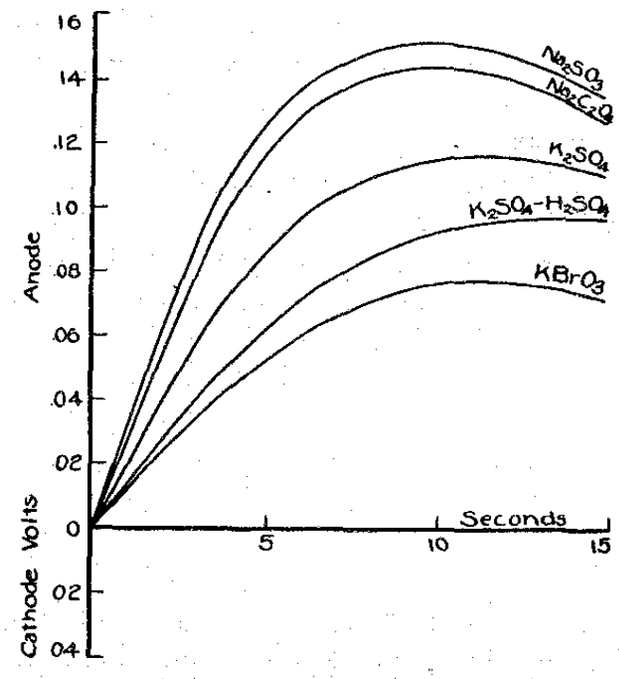


FIG. 3
Behaviour of copper sheet electrodes, uniformly coated with cuprous oxide and illuminated in oxidizing and reducing solutions.

3. The initial anode effect is more permanent when an oxidizing solution is in the cell. It is least permanent when a reducing solution is present.

4. In every case, removal of the light source after the illuminated electrode has become a cathode, shows an increase in the cathode tendency. The potential difference between the two cell electrodes then slowly returns to zero. This effect is indicated by the dotted portion of the curves. Minchin also mentioned this same effect in his report.

Before entering into the theoretical explanation of the behaviour of these cells, I shall present results obtained with electrodes in which local cell formation is minimized but not entirely removed. Such an electrode can be prepared by coating the copper sheet electrodes previously described, with a uniform and dense layer of cuprous oxide, but not insulating the back and unilluminated surfaces from the solution. The cuprous oxide was formed on copper sheet by the copper formate method as described by Garrison.

The curves shown in Fig. 3 show the results which were obtained with these sheet copper electrodes. The solutions used were 0.1 N as before.

These results may be summarized as follows:

1. The anode effect is magnified as the local cell formation is decreased.

2. The voltage maximum indicates that the local cell action is still appreciable and that even these electrodes would show a reversal in sign, if illuminated over a long period of time.

3. The anode effect is greatest in reducing solutions and least in oxidizing solutions.

4. The general shape of the time-volt curve for cells with sheet copper-cuprous oxide electrodes, is independent of the solution used.

I wish to propose the following theoretical explanation for the behaviour of the copper gauze-cuprous oxide, and copper sheet-cuprous oxide electrodes.

In all of these experiments, the behaviour of the cell under illumination was markedly different from the behaviour of illuminated cuprous oxide on platinum. Also, the general behaviour of these latter cells was independent of the solution used. We must, therefore, conclude that the change to a metallic copper electrode must provide the basis for all the altered behaviour. Either the copper itself influences the progress of the photochemical action or the local cell action on the face of the illuminated electrode has become a predominating factor.

Consider first the possible photochemical behaviour of cuprous oxide in contact with copper.

If we could set up an electrochemical cell of the type:

Cu	Solution	Cu_2O
(electrode)		(electrode)

it would seem logical to predict that the current would tend to flow in this cell solution from the copper to the cuprous oxide electrode. In other words metallic copper tends to reduce cuprous oxide and copper itself tends to be oxidized by cuprous oxide. If now, these two cell electrodes are brought together until they are in contact, the same tendency must still exist. The system produced by bringing into contact these two cell electrodes is exactly that system which we have in a dense and uniform layer of cuprous oxide placed on copper sheet. It follows that as far as photochemical tendencies are concerned, the cuprous oxide is in a reducing environment, exactly as if it were in contact with a reducing solution. I therefore conclude that illuminated cuprous oxide on copper tends to be photochemically reduced.

Consider now an ideal cuprous oxide-copper photovoltaic cell electrode, consisting of a molecularly uniform copper sheet, perfectly insulated at its back or unilluminated side, and uniformly covered upon its front surface by a continuous layer of cuprous oxide one molecule deep. Let two such electrodes be built up into a photovoltaic cell, and one electrode be uniformly illuminated:

Illuminated $Cu \mid Cu_2O$ Solution $Cu_2O \mid Cu$

No local cells can exist on the illuminated surface. The illuminated cuprous oxide in contact with copper is tending to be photochemically reduced. The illuminated cell is out of equilibrium and a potentiometer will show that the

illuminated electrode is tending to function as an anode, in order to bring the cell back into equilibrium. A constant photovoltage would be obtained which would be a direct measure of the photochemical reduction tendency of the illuminated cuprous oxide on copper. With a reducing solution in this cell the reduction tendency and the corresponding photovoltage will be increased; and with an oxidizing solution in this cell, the reduction tendency will be decreased and the corresponding photovoltage decreased.

The cuprous oxide-copper sheet electrodes, whose behaviour upon illumination is illustrated in Fig. 3, are approaching this ideal electrode just described. Their anodic photovoltage is weakened and inconstant through the formation of local cells. The anode tendency is greatest in reducing solutions and least in oxidizing solutions.

The thick and thin electrode film types first described by Becquerel,—"une couche mince d'iodide et une couche épaisse d'iodide,"—were really varying degrees of uniformity of layer of photosensitive substance on the metal electrode surface.

Local cells on the face of the illuminated electrode can possibly exist in the following forms:

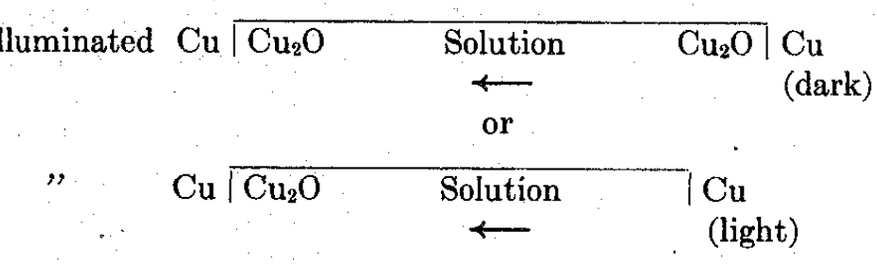
Cu | Cu_2O (light)	Solution	Cu_2O | Cu (dark)	(1)
Cu | Cu_2O (light)	Solution	| Cu (light)	(2)
Cu | Cu_2O (light)	Solution	| Cu (dark)	(3)
Cu | Cu_2O (very uniform and dense. Light)	Solution	Cu_2O | Cu (uniform and thin. Light)	(4)

On the sheet copper electrodes coated uniformly with cuprous oxide, the local cells formation similar to (1) would be expected to occur most commonly. On the gauze electrodes, pasted with cuprous oxide, any of these local cells might exist. Further, in the case of the copper sheet electrode, the local cell action may be considered as being comparatively small. There is a large internal resistance in each local cell, in this case, since local cell currents flowing between the front and back surfaces of the illuminated electrode must traverse an appreciable length of the cell solution.

A question at once arises in regard to the direction of flow of current in these local cells. In considering the behaviour of the photovoltaic cell with ideal electrodes free from local cells, it was found that the illuminated electrode possessed a negative charge as compared with the darkened electrode and current tended to flow in that direction which would equalize this difference of charges between the two electrodes. In these local cells now being examined, the two electrodes of the local cell are one and the same; they are identical with the massive illuminated electrode. There can be no difference

of charges between the two local cell electrodes. Since the whole existence of the local cell must depend upon a localized photochemical tendency of illuminated cuprous oxide to reduce, current will flow in the local cells to a point of illuminated cuprous oxide on copper from any other dissimilar point. The local cells are thus always tending to accommodate themselves to the photochemical reduction of cuprous oxide by copper.

If the various cell solutions used up to the present time are reviewed, it will be observed, that each of them in the local cells,



produces an irreversible electrode system. Since cuprous oxide is by postulation, always present in excess at a local cell cathode, it will be found that the local cells will only polarize anodically, with an increasing cuprous or cupric ion concentration at each local cell anode. It follows that, in all such cell solutions, the massive illuminated cuprous oxide-copper electrode, will ultimately obtain a surface polarized anodically, if local cell action is sufficiently large and time of illumination is sufficiently great. This explains the behaviour of the cuprous oxide-copper gauze electrodes, which initially showed a small anode tendency which was immediately overbalanced by an increasing anodic polarization of the local cells. This explanation also produces a complete solution of Minchin's reversal rule, previously cited. Even in the case of the gauze electrode systems, the initial anode effect though small, was appreciable and tended always to decrease the cathode effect produced by the anodically polarized local cells. As the light source was removed, the anodic polarization manifested in the cathodic effect in the massive illuminated electrode tended to apparently increase, as the initial anode effect of the illuminated massive electrode was at that moment completely removed. This explains the behaviour of the gauze electrode systems indicated in the dotted extension of the curves in Fig. 2.

It will be noted that the entire theory of this local cell action upon an illuminated electrode surface, has been built up with the idea that the solution in the local cell converted it into an irreversible cell system. It should be possible to select cell solutions that will throw these local cells into the class of completely reversible cells. If this can be done, the entire behaviour of the photovoltaic cell proper, may be expected to be again changed.

The best approximation to such solutions will be dilute neutral sodium chloride or sodium formate. A copper anode in such solutions tends to pass into solution as cuprous oxide, through an immediate hydrolysis of any cuprous chloride or cuprous formate formed.

The local cells,

$$\mathrm{Cu} \mid \overline{\mathrm{Cu_2O} \qquad \mathrm{NaCl} \qquad \mathrm{Cu_2O}} \mid \mathrm{Cu} \qquad (\leftarrow)$$

$$\mathrm{Cu} \mid \overline{\mathrm{Cu_2O} \qquad \mathrm{NaCO_2H} \qquad \mathrm{Cu_2O}} \mid \mathrm{Cu} \qquad (\leftarrow)$$

may be considered as being completely reversible, or nearly so.

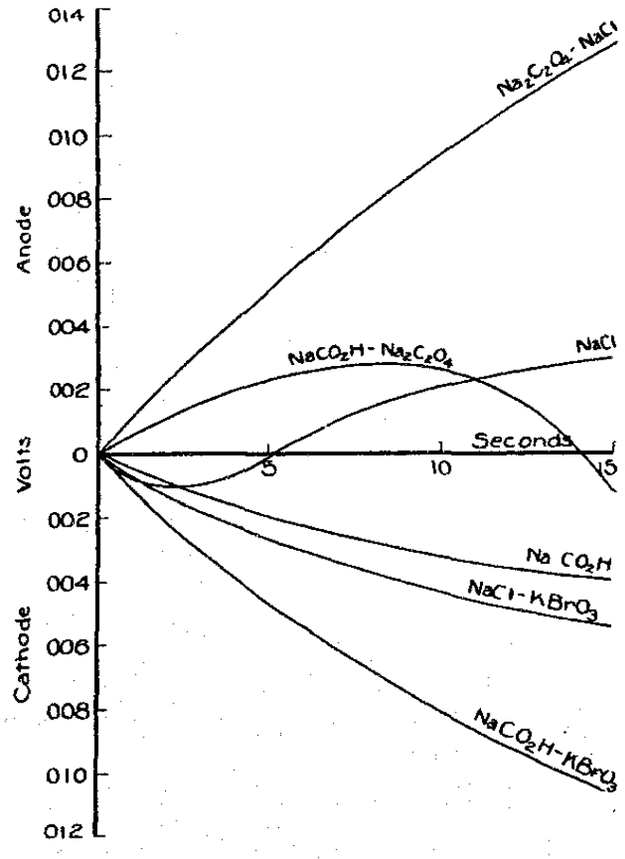


FIG. 4
Behaviour of copper gauze-cuprous oxide electrodes illuminated in solutions containing sodium chloride or sodium formate.

The results of illuminating both copper gauze and copper sheet electrodes coated with cuprous oxide, in these special solutions, and with these solutions combined with oxidizing or reducing agents, are shown in Figs. 4 and 5.

With a copper gauze electrode coated with cuprous oxide and illuminated in a photovoltaic cell, all local cell action on the exposed electrode surface will tend to be increased in sodium chloride or sodium formate cell solutions. No polarization occurs. The initial anode effect upon illumination will become negligible. If the local cells were completely reversible, no voltage difference whatever would be produced between the two massive cell electrodes. Under proper conditions the local cell,

$$\mathrm{Cu} \mid \overline{\mathrm{Cu_2O} \qquad \mathrm{NaCl}} \mid \mathrm{Cu} \qquad (\leftarrow)$$

would later produce cuprous oxide on all the exposed copper surfaces of the massive electrode and the massive electrode would be converted into a copper electrode uniformly coated with cuprous oxide, and behave upon illuminations as such. If this case is realized, the illuminated electrode will became anode in these special cell solutions. In reducing solutions, this effect will be most possible, since the efficiency of cuprous oxide formation may then be expected to be increased at the copper anode of the local cell. In an oxidizing solution the reverse thing will occur, the efficiency of cuprous

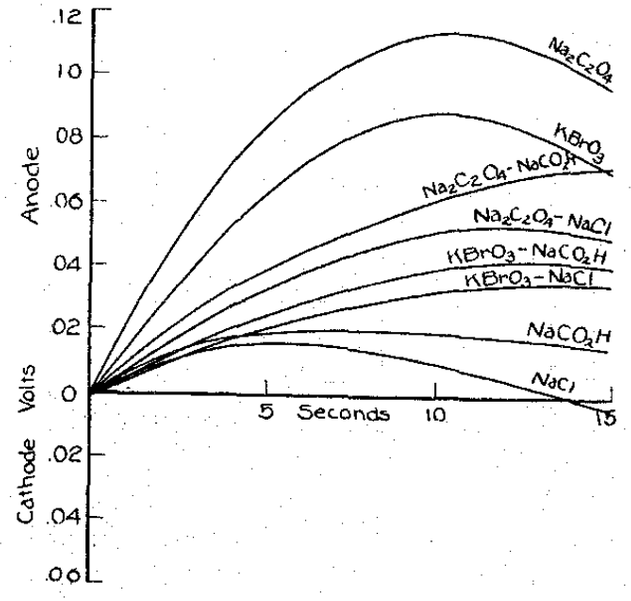


FIG. 5

Behaviour of copper sheet electrodes, uniformly coated with cuprous oxide and *illuminated in solutions containing* sodium chloride and sodium formate.

oxide formation at a local cell anode will decrease, and some cupric ions will pass into solution producing an anodic polarization, with a resulting cathodic tendency appearing in the illuminated massive electrode. Since dissolved atmospheric oxygen ordinarily will produce an oxidation tendency in a neutral solution, just as was postulated in considering the behaviour of cuprous oxide on platinum electrodes illuminated in neutral potassium sulfate solution; the ideal completely reversible local cell may not be attained in these neutral special solutions. The illuminated massive electrode will behave therefore, as a cathode in the neutral special solutions.

All of the above discussion dealt with the gauze electrodes, and an inspection of the corresponding experimental curves shown in Fig. 4 will indicate that the theory of the action of these special photovoltaic cells, agrees in general with the experimental results.

In the sheet copper electrodes uniformly coated with cuprous oxide, the local cell effect ordinarily, is of much less importance, since even when the local cells do exist on such an illuminated surface, they polarize themselves in most cell solutions. In these special cell solutions, however, the action of the local cells on the sheet electrode is greatly increased, and as a direct re-

sult, the original anode tendency of the illuminated massive electrode is correspondingly decreased. This fact is illustrated by the various experimental curves shown in Fig 5

The Cuprous Oxide-Copper Photovoltaic Cell with no Local Cell Formation

Finally, in order to bring out in the most convincing manner, the effect of local cells in decreasing the anode tendency of an illuminated copper electrode uniformly coated with cuprous oxide, the following trial was made. A copper sheet uniformly coated with cuprous oxide by the copper formate method was made the illuminated electrode in a photovoltaic cell, and the cell solutions were varied. The same electrode was then coated on its back or unilluminated surface with paraffine, and the photovoltages again measured in the same solutions. These results were obtained:

Solution	Uninsulated electrode	Insulated electrode
Sodium oxalate	.133 volts (anode)	.230 volts (anode)
Potassium sulfate	.118 " "	.215 " "
Potassium bromate	.105 " "	.210 " "

These varying values show at once that the photovoltages produced by an illuminated copper sheet-cuprous oxide electrode, may be widely varied as local cell formation on the illuminated surface is prevented.

The Silver Halide Photovoltaic Cells

The silver chloride, silver bromide, and silver iodide photovoltaic cells may be studied in the same manner as were the cuprous oxide cells. 0.1 N solutions were used in all cases, as before, unless otherwise specified. Since silver gauze was not available as an electrode material, all measurements of silver halide on silver and platinum electrodes, were made on sheet electrodes, of 3 × 8 cm. dimensions, with a copper wire folded into the silver sheet to permit ready attachment to the potentiometer. The method of observing the photovoltages, the cell arrangement, and light sources, were the same as in the cuprous oxide series.

The Silver Halide-Platinum Photovoltaic Cells

Silver chloride, bromide, and iodide, was made by adding silver nitrate in excess to the potassium halide salt solution, and washing the precipitate carefully with hot water by decantation.

It was found that this finely divided silver halide precipitate could be rubbed on a platinum surface as a moist paste and then allowed to dry in the air. An electrode prepared in this fashion possessed a layer of the halide upon its surface which adhered when the platinum was submerged in the cell solution.

As before, illumination of silver halide in the presence of an oxidizing solution, may be expected to result in a photochemical oxidation, with silver ion and the free halogen as the products of the light reaction. The silver halide-platinum electrodes, when illuminated, may be expected to behave in such a

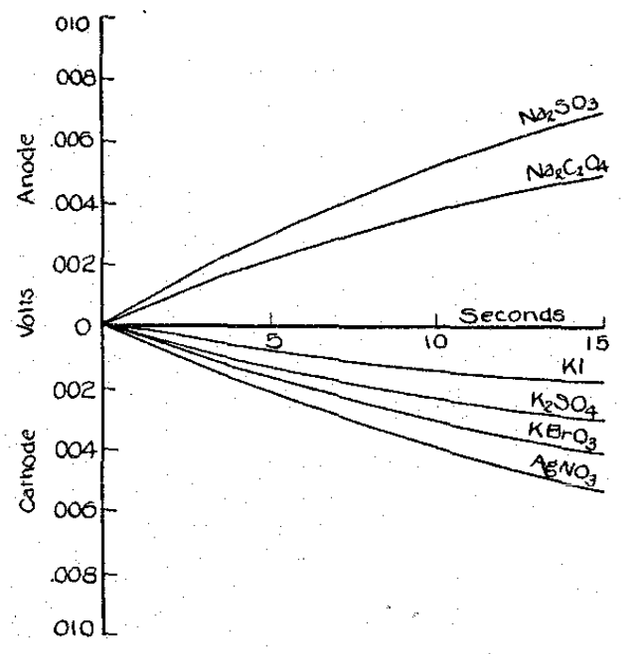


FIG. 6
Behaviour of platinum-silver iodide electrodes illuminated in different solutions.

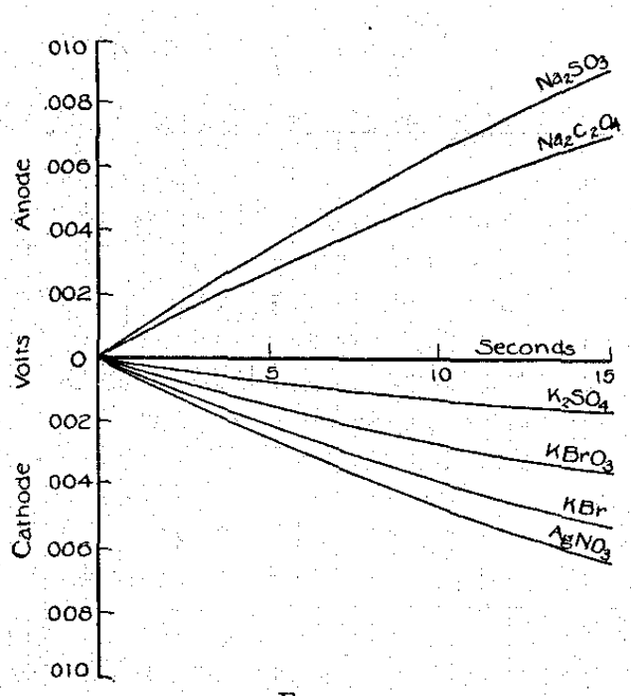


FIG. 7
Behaviour of platinum-silver bromide electrodes illuminated in different solutions.

way as will bring the illuminated and darkened portions of the cell into equilibrium. Illumination of this photovoltaic cell, with an oxidizing solution, may be expected then, to produce a reducing or cathode tendency in the illuminated electrode.

Conversely, silver halide illuminated in reducing solution, may be expected to undergo a photochemical reduction to metallic silver and halide ions. The illumination of this photovoltaic cell with a reducing solution, may be expected then, to produce an anode or oxidizing tendency in the illuminated electrode. The photo-current is tending to pass in that direction which will bring the two cell electrodes back into equilibrium.

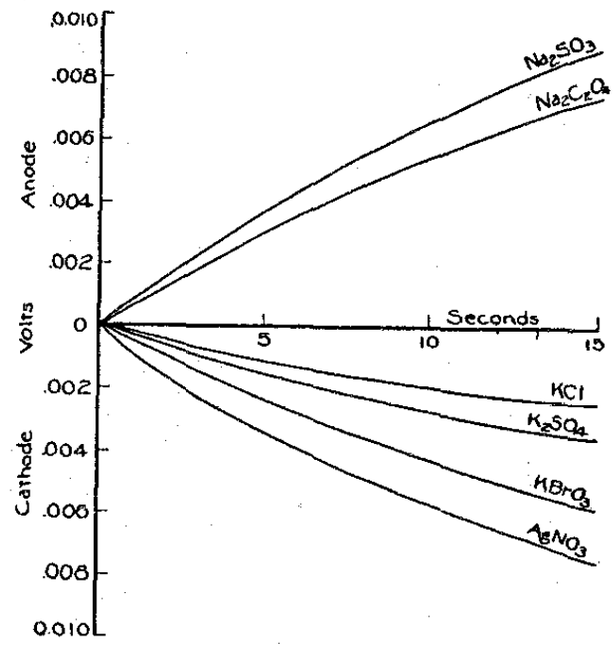


FIG. 8

[ ] Behaviour of platinum silver chloride electrodes illuminated in different solutions.

Figs. 6, 7, and 8, show the behaviour of the various silver halide-platinum electrodes, in different types of solutions. The abscissas and ordinates in these diagrams have the same significance as before.

The behaviour of these cells experimentally, was in accord with the theoretical requirements. In general the photovoltage of the silver chloride is greater than that of the silver bromide coated electrodes. The silver bromide cell photovoltage is in turn greater than that shown by the silver iodide cell. The observed differences were very small, however, and could not be accurately recorded in this method of electrode preparation and observation.

The Silver Halide-Silver Photovoltaic Cells

Since these preliminary experiments on the behaviour of illuminated silver halide on platinum indicate that the halides behave in the same general manner as did the cuprous oxide on platinum, we may expect the same general theories to apply when considering the silver halide on silver electrodes.

Silver halide illuminated while in contact with a silver sheet, should behave photochemically as though it were in a reducing environment; just as did cuprous oxide illuminated while in contact with copper. If the silver halide layer on the silver electrode surface is uniform and possible local cell formation is thereby minimized, the illuminated electrode tends to photochemically reduce and the two cell electrodes are not in equilibrium. The

tendency which the cell shows to return to an equilibrium is shown by an anodic behaviour of the illuminated cell electrode. As the possibility of local cell formation on the illuminated electrode is increased, this initial anode behaviour is decreased and may even be over-balanced by a cathode effect

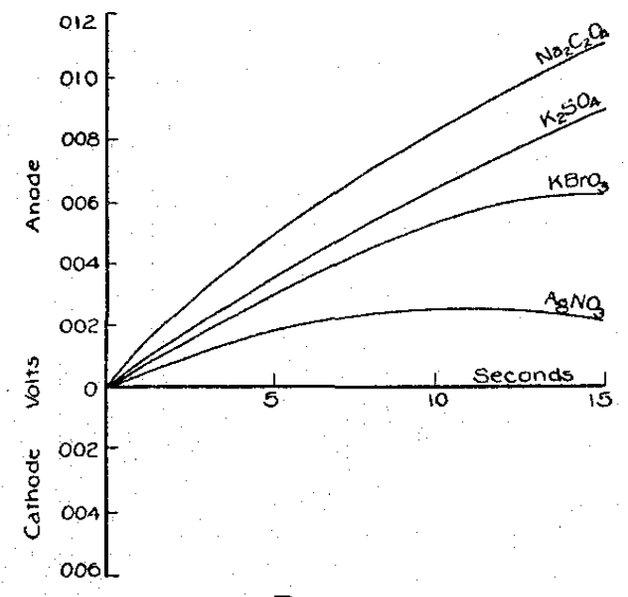


FIG. 9

Behaviour of silver sheet electrodes, uniformly coated with silver iodide, silver bromide, or silver chloride and illuminated in different solutions.

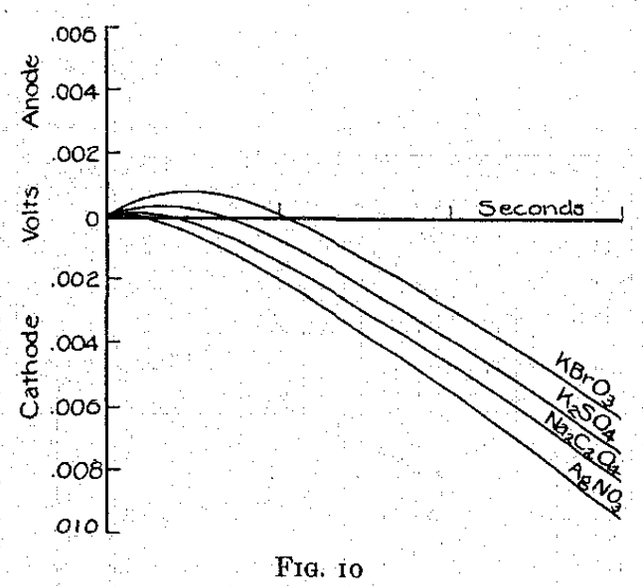


FIG. 10

Behaviour of silver sheet electrodes, not uniformly coated with silver iodide, silver bromide, or silver chloride and illuminated in different solutions.

produced through the anodic polarization of the irreversible local cells. If the corresponding sodium halide salt is used in the cell solutions, the local cells will become non-polarizable. Local cell action is correspondingly increased. In such a special cell solution, the initial anode effect of the illuminated massive electrode will be at a minimum, and if the silver halide formation were perfectly efficient at the local cell anodes, no photo-effect whatever would be observed at the initial moment of illumination. Actually,

this ideal case would be difficult to realize, since the reducing or oxidizing tendencies of the cell solutions will have a direct influence on the efficiency of the local cell actions.

The curves shown in Figs. 9, 10, and 11 illustrate the behaviour of these photovoltaic cells, and confirm this theoretical discussion.

With thick or uniform layers of the silver halide on silver, illuminated, the exposed electrode is initially anode in all ordinary solutions, tending to revert to a cathode as continued illumination breaks down the uniformity of the photosensitive layer.

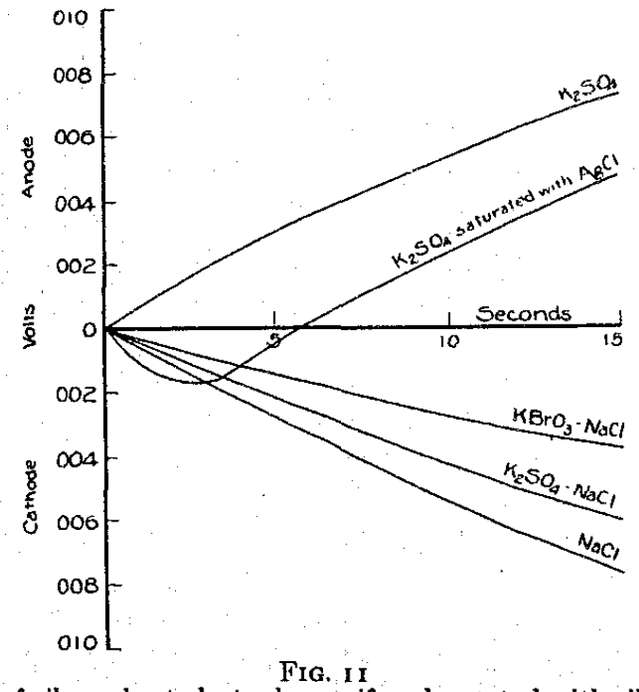


FIG. 11
Behaviour of silver sheet electrodes, uniformly coated with silver chloride and illuminated in solutions containing chlorides.

With thin or uniform layers of the silver halides on silver, illuminated, the exposed electrode is initially very slightly anodic but rapidly becomes cathodic.

With uniform or non-uniform layers of the silver halide on silver and illuminated in a halide solution, the local cells become reversible and the exposed massive electrode is always a cathode. The cathode effect becomes apparent, even if very small amounts aof halide salt are present in the solution, decreasing the initial anode effect produced in thick or dense layered electrodes in a reducing solution, and overbalancing the anode effect of a similar electrode illuminated in an oxidizing solution.

The sensitivity of the local cells upon the illuminated surface, to halide ions, is shown by the abnormal behaviour of a dense or uniform layered silver chloride electrode illuminated in a 0.1 N potassium sulfate solution saturated with silver chloride. Upon illumination an initial cathode effect is shown, because of the appreciable concentration of chloride ion present. As this chloride concentration is decreased by a constant precipitation of silver chloride at the local cell anodes, the illuminated electrode regains its normal behaviour and becomes an anode. The experimental curve obtained is shown in Fig. 11.

Summary

From this theoretical discussion and study of the behaviour of the cuprous oxide and silver halide photovoltaic cells, the following general rules can be set down, as a basis for explaining and predicting the behaviour of a given photovoltaic cell:

1. In a photovoltaic cell with two electrodes consisting of a photosensitive substance on platinum and dipping into an oxidizing solution, illumination will cause the exposed electrode to behave as a cathode, if the photosensitive substance present is tending to be photochemically oxidized when illuminated in contact with the same oxidizing solution.

If this same electrode system is dipped into a reducing solution, the illuminated electrode will behave as an anode, if the photosensitive substance is tending to be photochemically reduced when illuminated in contact with the reducing solution.

2. In a photovoltaic cell with electrodes consisting of the same metal from which the metallic constituent of the photosensitive material is derived, illumination tends to produce a photochemical reduction of the photosensitive substance.

3. If the photosensitive substance is on the illuminated electrode as a uniform layer, local cell formation on the illuminated surface will be at a minimum, and the exposed electrode will be an anode.

4. If the photosensitive substance is on the illuminated electrode as a non-uniform layer, local cells will be set up in the illuminated electrode. If these local cells tend to polarize, the illuminated electrode will eventually become a cathode after continued illumination. If these local cells do not polarize but are completely reversible, the electrical behaviour of the illuminated electrode will be determined by the oxidizing or reducing nature of the cell solution. In an oxidizing solution or a neutral solution the illuminated electrode will be a cathode while in a reducing solution, the illuminated electrode will be an anode.

If these local cells approach but do not attain complete reversibility, the illuminated electrode will be cathode in oxidizing or neutral solutions, and may or may not be cathode in reducing solutions.

Discussion of Recorded Photovoltaic Cells

The first photovoltaic cells made by Becquerel consisted of electrodes with each of the three silver halides; silver chloride, bromide and iodide, on platinum. The cell solution was in every case a dilute sulfuric acid. Since an acid solution may be considered as an oxidizing solution, the illuminated electrode in these cells should have been in every case a cathode. Becquerel obtained this result experimentally. Becquerel next found that uniformly coated silver halide-silver electrodes were always anode in this same acid solution, while non-uniformly coated electrodes were always cathode, upon illumination. In the first case, no local cells or a minimum of local cell action occurred upon the illuminated surface. The illuminated electrode was anode as a result of the cell reaction to a tendency toward a photochemical reduction of silver

halide. In the second case the local cell action was at a maximum on the illuminated electrode, and since these local cells in a sulfuric acid solution were anodically polarized, the illuminated electrode was a cathode.

Minchin next prepared silver halide-silver electrodes by drying an emulsion of the silver halide on the silver surface. This can be reasonably interpreted to mean that the silver halide was present upon the electrode surface in such a large amount, that the silver was completely coated with the photosensitive substance. In other words Minchin had made a uniformly layered electrode in which local cells upon the illuminated surface would be at a minimum. He found, however, that his illuminated silver chloride in a sodium chloride solution was on a cathode. His illuminated silver bromide on silver, in potassium bromide, also became cathode. This is as it should be, since the chloride and the bromide solutions increased any local cell action by converting these cells into non-polarizable types. The cathode effects produced by the local cells overbalanced the initial anode tendency of the illuminated electrode. In silver nitrate solution, his illuminated silver iodide-silver electrode, became anode. In this case the local cells polarized and had less influence upon the cell behaviour. The illuminated electrode was anode as a result of the cell reaction toward the photochemical reduction of the silver iodide.

The behaviour of the photovoltaic cells studied by Wildermann, is theoretically satisfactory. All of his photosensitive layers were of the non-uniform type. The illuminated electrode in all of his cells was a cathode.

The peculiar behaviour of the cuprous oxide-copper cell described by Case, should be readily explained. This cell was constructed as follows:

$$\text{Illuminated} \quad \text{Cu} \mid \overline{\text{Cu}_2\text{O} \qquad \text{Cu}(\text{CO}_2\text{H})_2\cdot\text{HCO}_2\text{H} \qquad \text{Cu}_2\text{O}} \mid \text{Cu}$$
$$\longrightarrow$$

Upon illumination of the photovoltaic cell, he found a current flowing in the solution, away from the illuminated electrode. Upon continued illumination with a closed circuit, the photovoltage slowly fell to zero. From Case's description of his electrodes, they consisted of a uniform layer of cuprous oxide on copper. Any local cells which may have been formed on the illuminated surface would polarize:

$$\text{Cu} \mid \overline{\text{Cu}_2\text{O} \qquad \text{Cu}(\text{CO}_2\text{H})_2\cdot\text{HCO}_2\text{H} \qquad \text{Cu}_2\text{O}} \mid \text{Cu}$$

Current passage through such a cell would result in the formation of cuprous oxide at the cell cathode, but the formic acid present would tend to prevent the formation of cuprous oxide at the cell anode. The resulting polarization of the local cell would allow the initial anode tendency of the illuminated massive electrode to predominate. However, with such a cell solution present, cuprous oxide would tend to be electrochemically precipitated on the darkened massive electrode, or cathode, as the current produced by illumination passed through the cell. At the same time cuprous oxide would be oxidized to copper formate at the anode, or illuminated massive electrode,

and through this removal of the photosensitive cuprous oxide, the photosensitivity of the cell will be decreased and eventually the photovoltage will drop to zero.

If the electrodes are now reversed and the formerly darkened electrode with its new coating of deposited cuprous oxide is illuminated, the cell photosensitivity will be regained and the entire process can be again repeated if the external circuit is kept closed.

Case noted that his cell electrodes behaved in a reverse manner in sodium chloride solution; the illuminated electrode was a cathode. It can be seen at once that a sodium chloride solution in the local cell,

$$\overline{Cu \mid Cu_2O \qquad NaCl \qquad Cu_2O \mid Cu}$$

will convert it into a reversible cell. Cuprous oxide is formed at the cell anode and destroyed at the cell cathode as current passes. This increased activity of the local cells upon the illuminated surface caused the original anode tendency to fall to zero and a cathode tendency to become apparent as a result of some slight anodic polarization in the local cells.

Garrison studied the effect of variation of density of cuprous oxide layer on copper. His results agree with those previously recorded in the experimental part of this paper.

Garrison also recorded the influence of hydrogen, hydroxyl, and cupric ions when added to the cell solution. He points out, however, that his study of the effect of varying the concentration of these particular ions, was made always on electrodes with an intermediate density or uniformity of layer,—that is, a layer which we now know may either produce an anode or cathode effect in the illuminated massive electrode, depending upon the character of the local cells in the illuminated surface. The general rules which he laid down for the behaviour of the copper-cuprous oxide photovoltaic cell as hydrogen, hydroxyl, and cuprous ion concentrations are varied, will not hold for all the possible densities or uniformities of cuprous oxide layer on copper.

Garrison confirmed by quantitative measurements, the effect of varying the density of the silver iodide layer on the silver electrode. He also accurately checked the behaviour of the cell as known amounts of potassium iodide or silver nitrate were added to the solution. Addition of silver nitrate was found to increase the anode tendency of an illuminated silver iodide-silver electrode; addition of potassium iodide to the cell solution increased the cathode tendency upon illumination. This is the correct behaviour of the cell in such solutions since variation of the solution is again varying the behaviour of the local cells in the illuminated cell electrode.

Acknowledgment

To Professor Wilder D. Bancroft, who by helpful suggestion, inspirational criticism, and personal direction, has made this study possible, I am sincerely grateful.

Cornell University

A CONVENIENT FORM OF APPARATUS FOR THE DETERMINATION OF MELTING TEMPERATURE*

BY GEORGE LYNN

Careful observations of the melting of some very pure organic substances[1] by the usual capillary tube method led to values of the melting temperature higher, frequently by more than 1°, and occasionally by as much as 3°, than determinations by means of the heating or cooling curve. The latter however yields the correct result, as shown by the fact that the values obtained by different observers working with different set-ups checked within less than 0.1°; it is therefore to be preferred to the capillary tube method, and can be carried out with equal convenience by use of the simple form of apparatus to be described. This is a modification of the apparatus described by Washburn,[2] by addition of an electric heating coil and of removable sample tubes, which increases its convenience and extends its range of usefulness; for it may be used to temperatures as high as 400°, for heating curves and boiling temperatures[3] as well as for the more usual cooling curves. The range below 0° can also be covered by immersion of the apparatus in a suitable low temperature bath. The amount of material required is of the order of 1 cc., but it is recoverable; but if temperature is measured by a thermoelement (which is preferable) a smaller tube may be used, and a much smaller sample suffices.

The apparatus, sketched in the figure, consists of a small unsilvered vacuum flask B, a heating coil H wound upon a glass tube, and the sample

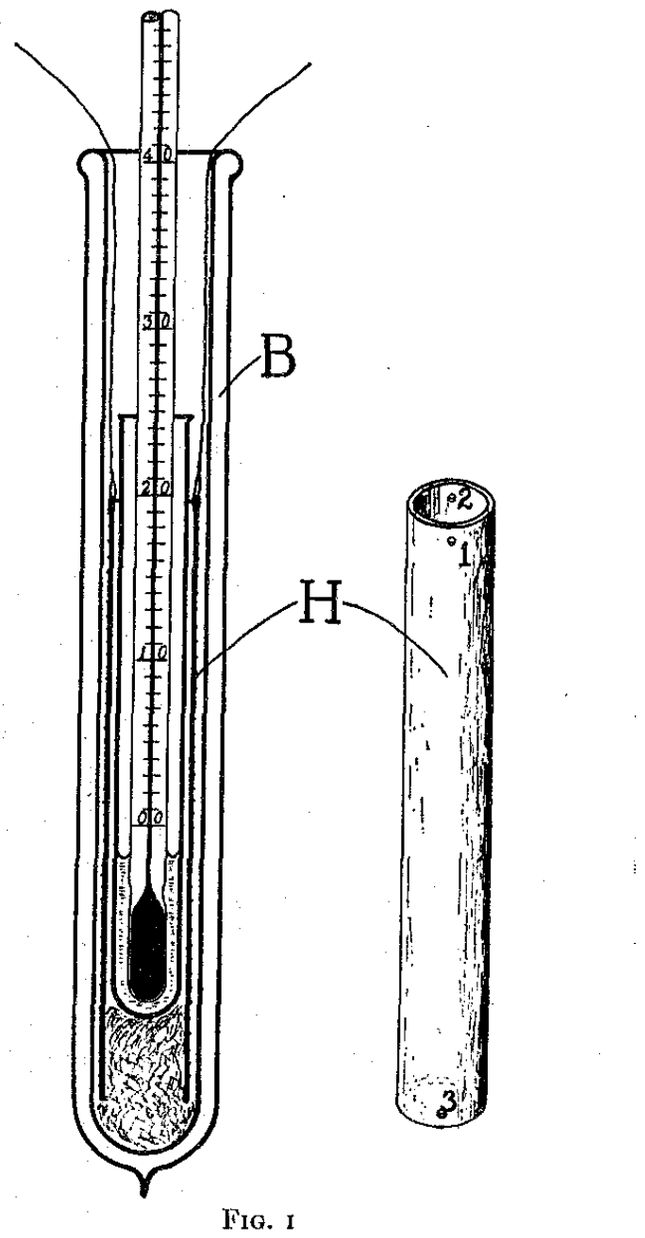


FIG. 1

* Contribution from the Department of Chemistry, Yale University.

[1] Cf. Andrews, Lynn and Johnston: J. Am. Chem. Soc., 48, 1274 (1926).

[2] E. W. Washburn: J. Ind. Eng. Chem., 16, 275 (1924).

[3] In this case the sample tube would be longer and project beyond the flask far enough to serve as a condenser.

tube which rests upon some glass wool; all glass parts are preferably made of pyrex. Their exact size is immaterial; those suggested are: flask 15 mm. inside diameter, 150 mm. deep; heater tube, 13 mm. outside diameter, 90 mm. long; sample tube 9 mm. inside diameter, 90 mm. long. In addition there is, of course, the rheostat necessary to control the current in the heating coil. The only part which requires further description is the heater coil, of #36 nichrome wire wound upon a glass tube in which three holes have been punched, as shown, by means of heated wire (of tungsten or nichrome). The fine wire is threaded several times through hole 3 in such a way as to hold in position the free end; approximately forty turns, about 2 mm. apart, are wound about the tube, and the other end threaded through hole 2 in such a way as to hold in place a copper wire which serves as one lead; the first free end is now brought up inside the tube and is used to fasten the second copper lead at hole 1.

To carry out a determination, material sufficient, when melted, to cover the bulb of the thermometer is put in the sample tube, which is then set in place, cotton being stuffed between the thermometer and vacuum flask; and an appropriate current is passed through the coil, so as to melt the substance. This current is now either cut off entirely—if the melting temperature is not too high—or set at a lower value, so as to give a satisfactory rate of cooling: the temperature readings taken at regular intervals, are plotted, supercooling being relieved, if necessary, by inoculation with a tiny crystal upon a glass thread. The flat on the curve is the melting temperature; its length, relative to the total period of freezing, is at the same time an excellent criterion of the purity of the substance.[1]

[1] Cf. W. P. White: J. Phys. Chem., **24**, 392 (1920); Andrews, Kohman, and Johnston: **29**, 914, 1048 (1925).

35 621

THE PHYSICAL CHEMISTRY OF COLOR LAKE FORMATION.
I. GENERAL PRINCIPLES

BY HARRY B. WEISER AND EVERETT E. PORTER

The adsorption of many dyes by wool, silk, and cotton is so weak that they are of value to the practical dyer only when used in connection with mordants. The term mordant (from mordre, to bite or to corrode) was first applied by the French to metallic salts which were supposed to act by biting or opening up a passage into the fibers of the cloth giving access to the color. Thus alum was believed to be effective in fixing certain dyes, owing to the solvent or corrosive action of the sulfuric acid. It is now known that the real mordant is the hydrous oxide and not the acid derived from the salt.

In general, a mordant may be defined as any substance that is taken up strongly by the fiber and in turn takes up the dye strongly. Two classes of mordants are generally recognized; acid, and basic or metallic. The acid mordants are the tannins, the fatty acids, albumin, hydrous silica, arsenic acid and phosphoric acid, while the basic mordants are the hydrous oxides of the heavy metals, the most important of which are the hydrous oxides of chromium, aluminium, iron, tin, and copper in the order named.

In dyeing a mordanted cloth it is, in most cases, the mordant rather than the fiber which takes up the dye. When a dye is taken up by a mordant in the absence of a fiber, the complex is called a color lake. This investigation deals with the mechanism of the formation of color lakes of the hydrous oxides of iron, chromium and aluminum as lake bases.

For a long time all such color lakes were believed to be definite chemical compounds between the dye and the mordant. This view was questioned by Biltz and Utescher[1] who investigated the behavior of alizarin with the hydrous oxides of chromium and iron. With the former, the amount of dye taken up increased continuously with increasing concentration of solution, giving no indication whatsoever of the formation of chromium alizarate. With hydrous ferric oxide, on the other hand, the amount of dye taken up increased so rapidly with relatively small changes in the concentration of the bath, that Biltz was lead to assume the formation of a ferric alizarate. More recently Bull and Adams[2] investigated the iron-alizarin lake and concluded that it is a ferric oxide-sodium alizarate complex. Marker and Gordon[3] studied the influence of hydrogen ion concentration on the amount of the basic dyes, crystal violet and methylene blue, and the acid dyes, orange II and metanil yellow, taken up by ferric oxide, alumina, and silica. In most instances, breaks were obtained in the pH-adsorption curves which were interpreted to mean that chemical compounds were formed between the hydrous oxides and

[1] Ber., **38**, 4143 (1905).
[2] J. Phys. Chem., **25**, 660 (1921).
[3] Ind. Eng. Chem., **16**, 1186 (1924); **15**, 818 (1923).

the dyes investigated. As we shall see, the value of Marker and Gordon's paper would seem to lie chiefly in their recognition of the importance of hydrogen ion concentration in color lake formation rather than in the data submitted or the conclusions drawn therefrom.

In the light of our observations[1] on adsorption of ions from a mixture of electrolytes, it would seem that the concentration of the ions present in the dye bath, including hydrogen and hydroxyl, might be quite as important in determining the composition of a color lake as the concentration of the dye itself. Moreover, the nature, physical character, and purity of the mordant would be expected to influence the composition of the lake. In order to determine the effect of each of the several factors on the lake-formation process, the first investigations were made on systems in which all the variable constituents could be determined quantitatively. To simulate the conditions of lake formation as nearly as possible, observations were made at varying hydrogen ion concentrations on the taking up of the inorganic anion, sulfate, and the organic anion, oxalate, both separately and simultaneously, by highly purified hydrous oxides of known composition. The results of these observations are recorded in this communication. In the subsequent papers the observations will be extended to the true color lakes.

Experimental Procedures

The Adsorbent. In most of the earlier investigations on adsorption of the dyes by the hydrous oxides, the latter were precipitated from the respective salt solution with ammonia, washed by decantation, and dried. A weighed amount of the adsorbent prepared in this way was shaken with the dye and the amount taken up was determined from the change in the concentration of the solution. This method of procedure is open to certain objections: first, it is impossible to obtain equilibrium conditions in a reasonable length of time; second, it is impossible to get absolutely uniform samples; and third, the purity of the oxides is uncertain.

To obviate these difficulties, the hydrous oxides used in the present investigation were prepared in the form of sols. This was done by precipitating the gels from the respective chloride solutions with ammonia, washing by decantation with the aid of the centrifuge until peptization began, and finally, peptizing with the smallest possible quantity of hydrochloric acid. The sols formed in this way were dialyzed in boiling solution for approximately one hundred hours according to the method of Neidle,[2] using a five-liter balloon flask to replace the open beaker. The rate of flow of water was kept at about two liters per hour. By this procedure, products were obtained having a much higher degree of purity than the precipitated gel.

Determination of Adsorption. Two methods may be employed for determining the adsorption by the gel thrown down on the addition to the sol of a given amount of electrolyte: the gel may be washed by the aid of the centri-

[1] Weiser: J. Phys. Chem., **30**, 20, 1527 (1926).
[2] J. Am. Chem. Soc., **39**, 71 (1917).

fuge and the analysis made on the supernatant liquid with all the wash water; or an aliquot part of the supernatant liquid may be pipetted off and analyzed, calculating the adsorption from the change in concentration. From the results of a number of preliminary experiments, it was found that the latter method gives more reliable and consistent results. The errors eliminated by using this method are the differences in the conditions of washing and the variation in the reversibility during washing. The latter factor is especially important since the adsorption is reversible in all cases, equilibrium between the wash water and the precipitate being established more or less rapidly. The error introduced by the failure to take into account the volume occupied by the solid is kept small, amounting to less than one tenth of one percent in most cases. The fact that this error is constant in any series of experiments, reduces still further any objection to the method.

The mixing of the hydrous oxide sol with the electrolyte was done in 250 cc wide-mouth bottles with ground-glass stoppers. The solution to be mixed with the sol was put in the bottle and diluted to exactly 150 cc. Fifty cubic centimeters of sol containing the desired amount of hydrous oxide, was placed in a 60 cc bulb with a large neck inserted through a rubber stopper which fitted the bottle. In order to retain the sol when the bulb was inverted, the neck of the latter was fitted with a thin slice of rubber cut from a stopper. To mix the solutions, the stopper with the bulb was inserted in the bottle which was given a quick jerk thereby dislodging the thin stopper from the neck of the bulb and allowing very rapid and thorough mixing of the solutions. Numerous tests showed that equilibrium between the adsorbent and the adsorbate was established almost at once. However, the mixtures were allowed to stand in the glass-stoppered bottles for about 24 hours after which they were centrifuged and an aliquot part withdrawn for analysis. The hydrogen ion concentration was determined in the supernatant liquid as well as in a similar mixture in which water was substituted for the sol. The former determinations are designated in the tables as "pH after adsorption" and the latter as "pH before adsorption." Since the sol is approximately neutral, if the small error introduced by the space occupied by the solid particles of the oxide is neglected, the difference between the two pH values is the change due to the adsorption by the colloidal particles.

Hydrogen Ion Concentration. The hydrogen ion concentrations were measured throughout with the hydrogen electrode. The apparatus employed was the Leeds and Northrup "Type K" potentiometer in connection with one of their sensitive galvanometers. A small electrode vessel of special design requiring but 4 cc of solution for a determination, was used. The gas entered the electrode vessel at the bottom through a very small capillary, a pressure of seven to eight centimeters of mercury being required to cause a flow of one cubic centimeter of gas each three seconds. This served to agitate the liquid very effectively without blowing it out of the vessel. The electrodes were prepared by platinizing 4-millimeter glass tubes to a height of 1 centimeter. These electrodes come to equilibrium more quickly than the platinized

platinum electrodes and are easily and economically renewed. The hydrogen used was purified by conducting it over hot platinized asbestos, bubbling through potassium hydroxide, sulfuric acid, and finally through water at the same temperature as the electrode vessel.

The Adsorption of Sulfate

Adsorption Experiments. The adsorption of sulfate by a constant amount of chromic oxide was determined at varying hydrogen ion concentrations, according to the procedure described above. In all the experiments, the initial sulfate concentration was maintained constant at 0.005 normal, while the pH value was varied through wide limits using suitable proportions of sulfuric acid, potassium sulfate, and potassium hydroxide. Obviously, this procedure introduces varying amounts of potassium ion as well as of hydrogen and hydroxyl ions. This effect may be considered as negligible, since it was found in some experiments to be recorded in a subsequent paper, that very little or no alkali ion is adsorbed under similar conditions. If the alkali adsorption were appreciable, it would serve to increase the adsorption of the negative ions. It should be pointed out that the same initial concentration of sulfate leads to a varying equilibrium concentration. Since the final concentration is smaller the greater the adsorption, it follows that the variations in the adsorption values would have been somewhat larger than those observed if the final concentration had been kept constant. However, the final concentration is sufficiently large in all cases to put the adsorption well on the flat of the isotherm.

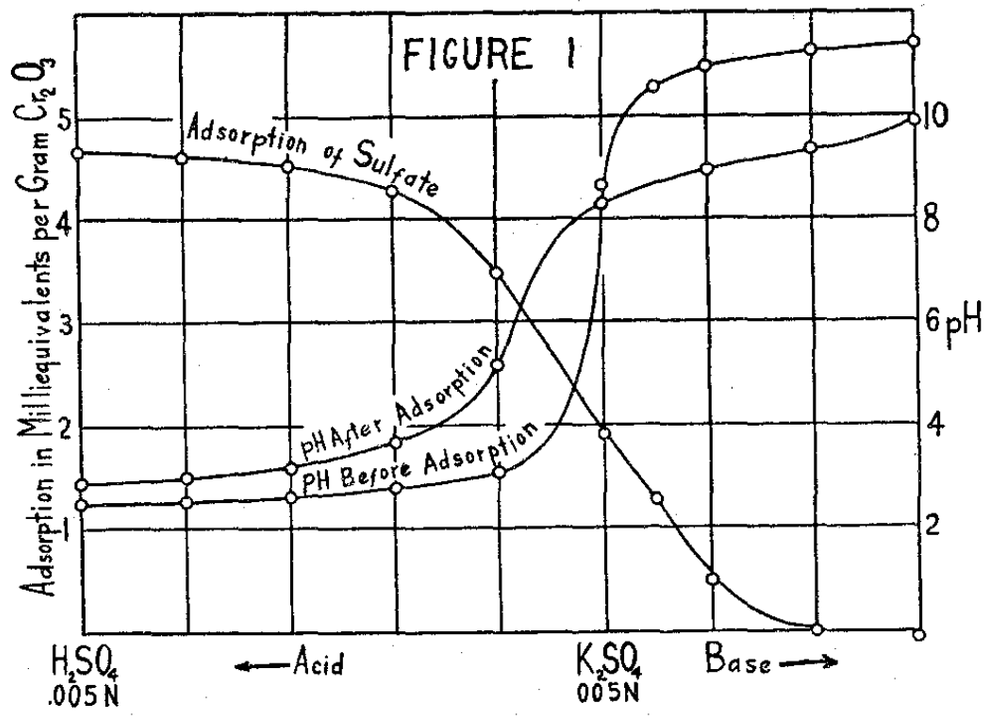
The marked effect of the hydrogen and hydroxyl ions on the adsorption of sulfate is shown by the data recorded in Table I and shown graphically in Fig. 1. It will be seen that raising the concentration of the hydrogen ion increases the positive charge on the particles, thereby increasing their capacity

TABLE I

Adsorption of Sulfate by Hydrous Chromic Oxide at varying pH Values

Cc of soln. mixed with 50 cc of sol containing 0.125 grams of Cr_2O_3 in a total of 200 cc			Adsorption values milli-equiv. per gram Cr_2O_3	pH values	
N/50 H_2SO_4	N/50 K_2SO_4	N/50 KOH		Before adsorption	After adsorption
50	0	0	4.66	2.42	2.87
40	10	0	4.60	2.49	2.97
30	20	0	4.52	2.59	3.15
20	30	0	4.28	2.73	3.64
10	40	0	3.48	3.09	5.15
0	50	0	1.90	8.68	8.29
0	50	5	1.28	10.61	8.73
0	50	10	0.48	10.95	8.96
0	50	20	−0.08	11.28	9.39
0	50	30	−0.10	11.4⁻	9.87

to adsorb sulfate. The adsorption of the sulfate falls off quite rapidly with increasing concentration of the hydroxyl ion, the carrying down of the sulfate being completely nullified at a pH value of about 9.2. It is obvious however that both sulfate and hydroxyl are adsorbed in the alkaline range from a pH of 7 to 9. In Loeb's investigations on the proteins[1] it seems probable that he overlooked the specific effect of cations other than hydrogen and of anions other than hydroxyl since he worked with relatively low concentrations of salts.



The pH-adsorption curve is smooth throughout, showing no indication of the formation of a compound between the sulfate and the hydrous oxide even at pH values as low as 2.0.

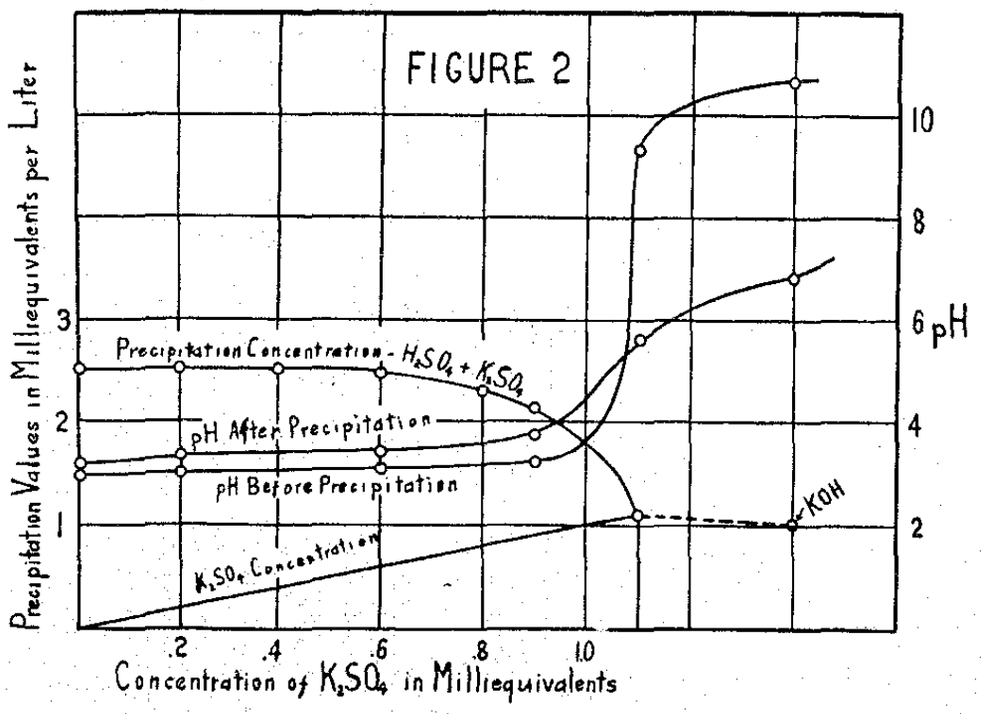
TABLE II

Precipitation of Chromic Oxide Sol with Sulfate at varying pH Values

Cc of soln. mixed with 5 cc of sol containing 0.0125 grams of Cr_2O_3 in a total of 20 cc			Precipitation values milli-equiv. per liter of mix	pH values	
N/50 H_2SO_4	N/50 K_2SO_4	N/50 KOH		Before adsorption	After adsorption
2.50	0.0	0.0	2.50	2.92	3.16
2.30	0.2	0.0	2.50	3.00	3.30
2.10	0.4	0.0	2.50		
1.85	0.6	0.0	2.45	3.07	3.38
1.50	0.8	0.0	2.30		
1.25	0.9	0.0	2.15	3.18	3.74
0.00	1.1	0.0	1.10	9.35	5.61
0.00	0.0	1.0	1.00	10.67	6.85

[1] "Proteins and the Theory of Colloidal Behavior" (1922).

Precipitation Experiments. Some observations on the precipitation value of sulfate ion at varying pH values were next made. 5 cc of the sol was placed in the inside compartment of a mixing apparatus[1] made entirely of glass, and varying amounts of potassium sulfate, sulfuric acid, and potassium hydroxide diluted to exactly 15 cc were placed in the outside compartment. These solutions were mixed rapidly, allowed to stand for about 24 hours, and centrifuged to determine the presence or absence of complete precipitation. The pH values were determined for the supernatant liquid as well as for like mixtures substituting water for the colloid. The results are given in Table II and represented graphically in Fig. 2.



It should be noted that the precipitation value for potassium hydroxide alone is 1.0 milliequivalent per liter as compared with 1.1 for the potassium sulfate. If we make the usual assumption that the relative amounts required for precipitation are a measure of the adsorbability of the two ions, this would mean that hydroxyl is adsorbed only a little more strongly than sulfate. This is not in accord with the facts, for it was found that no measurable amount of sulfate is adsorbed from a solution in which the concentration of hydroxyl is 0.00016 when the concentration of sulfate is 0.005. However, the adsorption of sulfate ion or hydroxyl ion is sufficiently strong that but little of either remains in solution at their respective precipitation values. This is especially true in the case of hydroxyl ion, the pH value of the supernatant liquid after precipitation with potassium hydroxide being 6.85 which is approximately that of pure water. It will be noted that the stability is not increased by further addition of acid after the final pH value of the mixture has reached 3.4 which brings the hydrogen adsorption to the flat of the isotherm. In Fig. 1 it will be seen that the sulfate has attained its maximum adsorption at

[1] Weiser and Middleton, J. Phys. Chem. **24**, 48 (1920).

the same pH value, illustrating that maximum adsorption of the precipitating ion corresponds with maximum stability of the sol. The course of the curves demonstrates clearly the truth of the time-honored assumption that the stabilizing action on the acid side is due to the adsorption of hydrogen ions, and the precipitating action of the KOH is due to neutralization by adsorption of the hydroxyl ions.

The Effect of Calcium Ion. In view of the marked effect of hydrogen on anion adsorption, one would expect a similar effect for other cations that are strongly adsorbed. The adsorptions of sulfate by hydrous chromic oxide from solutions of potassium sulfate and of calcium sulfate of the same equivalent concentrations were compared. From potassium sulfate, the adsorption was 1.86 milliequivalents at a pH of 7.32, while from calcium sulfate the adsorption was 2.23 at a pH of 7.39. This suggests that one could determine the effect of varying calcium ion concentration on the adsorption at constant pH values. In a subsequent paper on the alizarin lakes this behavior will be shown to be of particular significance. We should not expect the calcium ion to have a very marked effect in the acid range because it is so much less adsorbed than hydrogen. On the other hand, the effect should become large in neutral and basic range on account of the low concentration of the hydrogen ion.

Adsorption of Oxalate

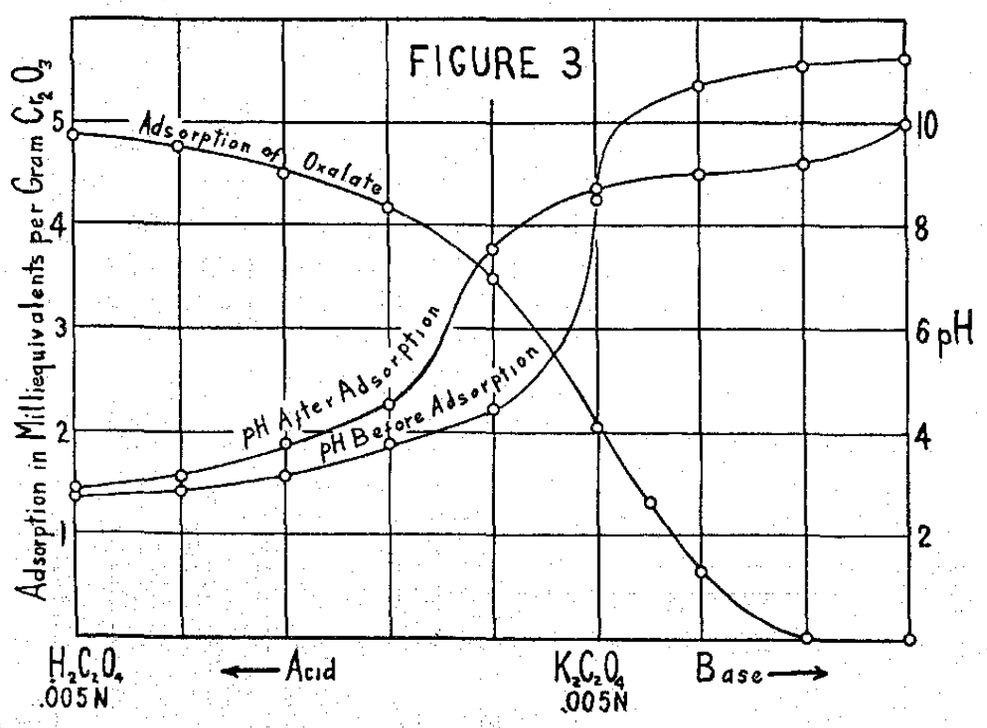
Adsorption by Hydrous Chromic Oxide. Experiments similar to those described above for sulfate were carried out for oxalate. The results are tabulated in Table III and shown graphically in Fig. 3. The form of the oxalate curve is strikingly similar to that of the sulfate curve throughout the entire range. The difference in the pH values before and after precipitation is greater in the case of oxalate than of sulfate due to stronger adsorption of

TABLE III

Adsorption of Oxalate by Hydrous Chromic Oxide at varying pH Values

Cc of soln. mixed with 50 cc of sol containing 0.125 grams of Cr_2O_3 in a total of 200 cc			Adsorption values milli-equiv. per gram Cr_2O_3	pH values	
N/50 $H_2C_2O_4$	N/50 $K_2C_2O_4$	N/50 KOH		Before adsorption	After adsorption
50	0	0	4.88	2.73	2.89
40	10	0	4.77	2.87	3.16
30	20	0	4.47	3.16	3.78
20	30	0	4.17	3.81	4.56
10	40	0	3.48	4.45	7.54
0	50	0	2.06	8.56	8.73
0	50	5	1.32	10.58	8.99
0	50	10	0.65	10.67	9.20
0	50	20	0.00	11.12	9.48
0	50	30	0.06	11.23	9.99

oxalate ion which is accompanied by a corresponding increase in the adsorption of hydrogen ion. The fact that the quantity of oxalate adsorbed is a little less than of sulfate in the range of total acid around 0.0015 normal is not an exception to the above statement. The primary and secondary ionization constants for the two acids are as follows: H_2SO_4, $K_1 = 0.450$, $K_2 = 0.017$; $H_2C_2O_4$, $K_1 = 0.100$, $K_2 = 0.00005$. It is obvious that at the normality under consideration, the concentration of the divalent oxalate is considerably less than that of divalent sulfate. Moreover, there is a considerable difference in the hydrogen ion concentration of the two solutions as is indicated by the greater pH value of oxalic acid as compared with sulfuric. In the section on the simultaneous adsorption of oxalate and sulfate are graphs which show this



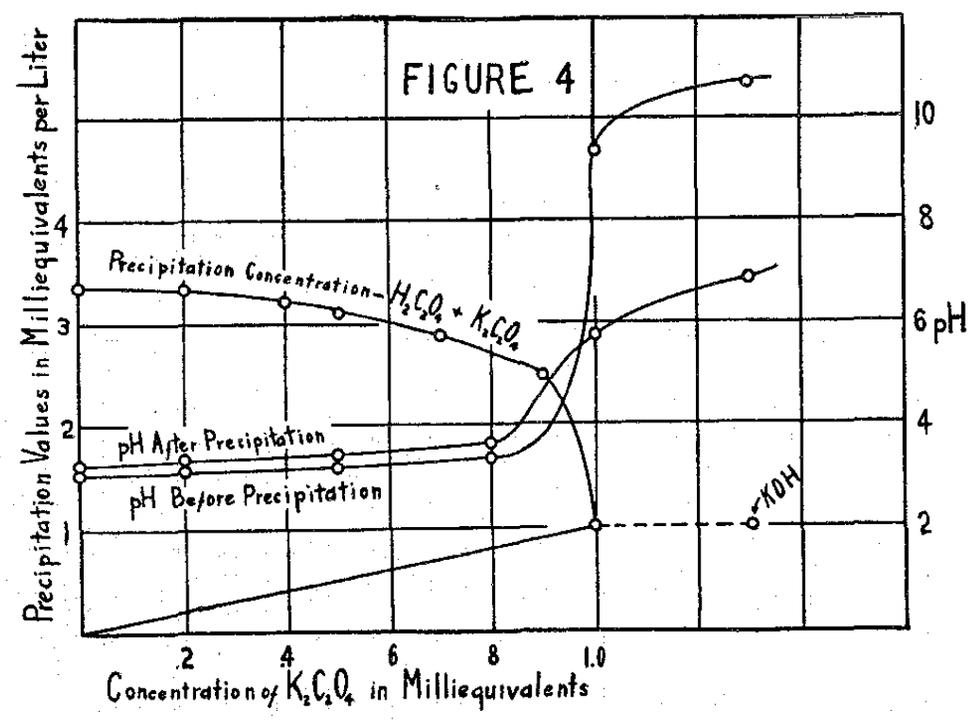
same effect. On the other hand, at the same hydrogen ion concentration, the adsorption of oxalate is greater than that of sulfate throughout the entire range investigated. There is no way of telling just what part of the adsorption is bioxalate or bisulfate but it is evident that a considerable quantity of bioxalate is adsorbed in the acid range.

Precipitation Experiments. In Table IV and Fig. 4 the relation between the hydrogen ion concentration and the precipitation value of oxalate is shown. It will be noted that the precipitation value for oxalate is less than for sulfate at pH values between 6 and 9, a behavior which would be considered normal since oxalate is adsorbed more strongly than sulfate. On the other hand, at pH values less than 5 the precipitation value of oxalate exceeds that of sulfate although the adsorption of oxalate still continues greater than sulfate. This apparent discrepancy is due to the fact that the secondary ionization of oxalic acid is but 1/350 of that of H_2SO_4. It is obviously erroneous, therefore, to assume that equal concentrations of sulfate and oxalate give equal concentrations of the strongly adsorbed divalent ions. In the case of oxalate the

TABLE IV

Precipitation of Chromic Oxide Sol with Oxalate at varying pH Values

Cc. of soln. mixed with 5 cc of sol containing 0.0125 grams of Cr_2O_3 in a total of 20 cc			Precipitation values milli-equiv. per liter of mix	pH values	
				Before adsorption	After adsorption
N/50 $H_2C_2O_4$	N/50 $K_2C_2O_4$	N/50 KOH			
3.35	0.0	0.0	3.25	3.05	3.19
3.15	0.2	0.0	3.35	3.11	3.32
2.80	0.4	0.0	3.20		
2.60	0.5	0.0	3.10	3.17	3.40
2.20	0.7	0.0	2.90		
2.00	0.8	0.0	2.80	3.38	3.51
1.60	0.9	0.0	2.50		
0.00	1.0	0.0	1.00	9.40	5.79
0.00	0.0	1.0	1.00	10.67	6.85



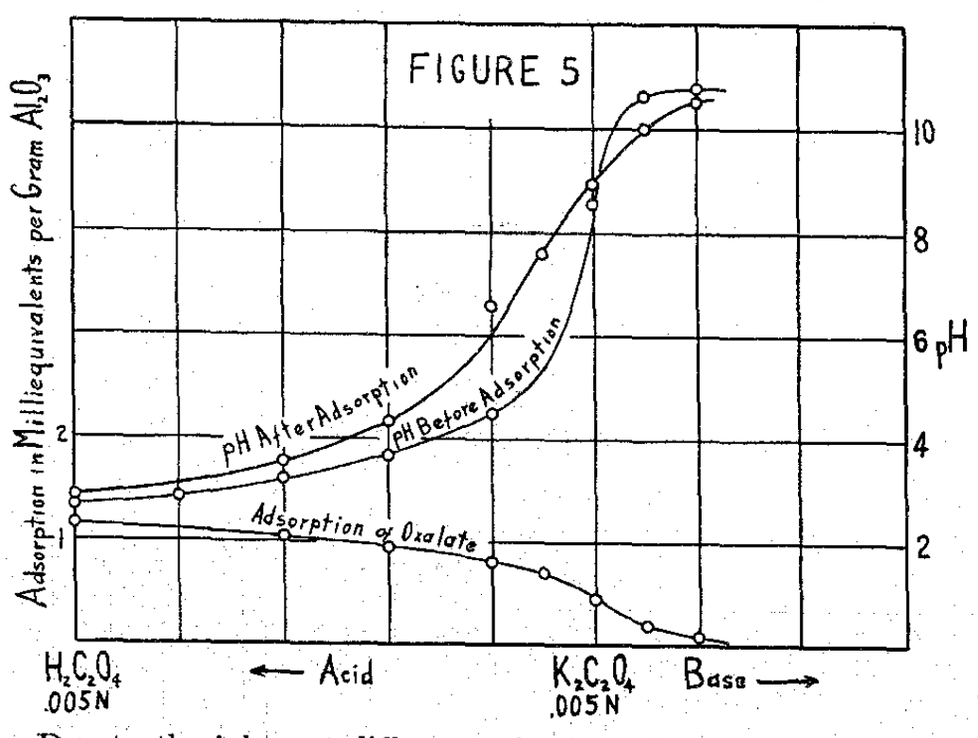
actual concentration of the divalent ion, which is a measure of its effective concentration, is but a small fraction of the total concentration in the acid solution. Hence the equivalent adsorption of oxalate appears to be greater than that of sulfate since a larger percentage of the former is adsorbed as the univalent bioxalate ion and is expressed as if all of it were adsorbed as the bivalent ion.

Attention should be called to Weiser and Middleton's[1] observation that the precipitation value of sulfate was less than that of oxalate for a Crum's alumina sol although the adsorption of oxalate by the precipitated gel was

[1] J. Phys. Chem., **24**, 630 (1920).

greater than that of sulfate. Since the Crum sol was quite acid this anomalous behavior is readily understood. Thus, the precipitation value in milliequivalents per liter of sulfate in neutral solution is 1.1 and that of oxalate is 1. This is the reverse of the order of adsorption, as it should be. On the other hand, when the hydrogen ion concentration is as great as 0.0001 normal, the order of precipitation values is reversed.

Adsorption by Hydrous Ferric Oxide and Aluminum Oxide. The data for the adsorption of oxalate by hydrous ferric oxide and by alumina are given in Tables V and VI and represented graphically by Figs. 5 and 6. As one might expect the effect on adsorption of varying the hydrogen ion and hydroxyl ion concentrations is similar to that observed with the hydrous chromic



oxide. Due to the inherent differences in the colloids, the total quantity is different for each oxide but the general character of the pH-adsorption curves is the same.

TABLE V

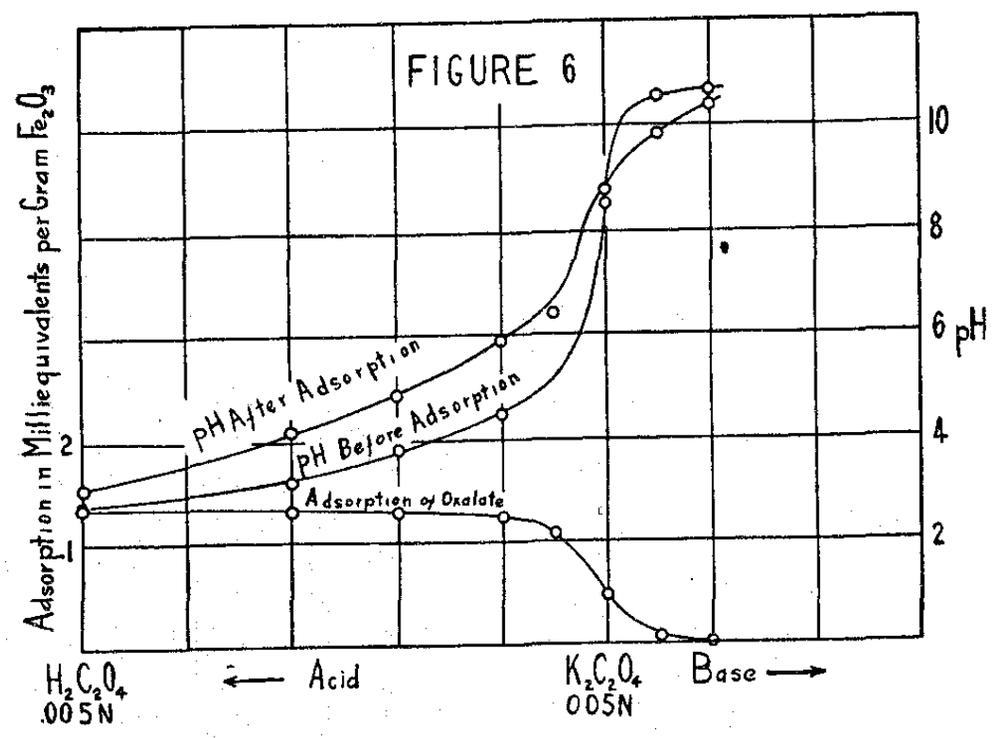
Adsorption of Oxalate by Hydrous Aluminum Oxide at varying pH Values

Cc of soln. mixed with 50 cc of sol containing 0.0845 grams of Al_2O_3 in a total of 200 cc			Adsorption values milli-equiv. per gram Al_2O_3	pH values after adsorption
N/50 $H_2C_2O_4$	N/50 $K_2C_2O_4$	0.037 N KOH		
50	0	0	1.20	2.82
30	20	0	0.99	3.45
20	30	0	0.94	4.35
10	40	0	0.76	6.62
5	45	0	0.69	7.58
0	50	0	0.43	8.92
0	50	5	0.16	10.08
0	50	10	0.11	10.58

TABLE VI

Adsorption of Oxalate by Hydrous Ferric Oxide at varying pH Values

Cc of soln. mixed with 50 cc of sol containing 0.132 grams of Fe_2O_3 in a total of 200 cc			Adsorption values milli-equiv. per gram Fe_2O_3	pH values after adsorption
N/50 $H_2C_2O_4$	N/50 $K_2C_2O_4$	0.0.037 N KOH		
50	0	0	1.32	3.09
30	20	0	1.31	4.18
20	30	0	1.29	4.74
10	40	0	1.25	5.92
5	45	0	1.08	6.32
0	50	0	0.46	8.79
0	50	5	0.07	9.84
0	50	10	0.00	10.42
0	50	20	peptized	



Simultaneous Adsorption of Sulfate and Oxalate

Observations on simultaneous adsorption by hydrous oxides have been made by Mehrotra and Sen[1] and by Miller.[2] The former studied the mutual effects of copper and barium in varying proportions on their relative adsorption by hydrous manganese dioxide. Since no account was taken of the hydrogen ion concentration to which hydrous manganese dioxide is quite sensitive, their results are of questionable value. Data in one specific case led them to the general conclusion that "The sum of the adsorption of two ions from a mixture is always greater than the adsorption of either of them present alone in the solution." Reference to Table VIII as well as to Table IX and

[1] J. Indian Chem. Soc., 3, 397 (1926).

[2] U. S. Public Health Reports, 39, 1502 (1924).

Figs. 7 and 8 will show that this is not true in every case, and it may not be true in any case, provided the precipitations take place under the same conditions.

Some of the data obtained by Miller on the simultaneous adsorption of oxalate and sulfate by hydrous alumina are reported in Table VII. On the

TABLE VII

Simultaneous Adsorption of Sulfate and Oxalate by Al_2O_3 (Miller).

Before precipitation		At equilibrium after precipitation			
Molar concentration K_2SO_4	Molar concentration $K_2C_2O_4$	K SO_4 solution / SO_4 precipitate	K C_2O_4 solution / C_2O_4 precipitate	Sum of mols of C_2O_4 + SO_4 per mol of Al in precipitate	pH
0.0500	0.0500	1,220.0	0.473	0.1819	8.8
0.0650	0.0350	11.2	0.340	0.1916	8.3
0.0750	0.0250	14.0	0.226	0.1926	8.1
0.0875	0.0125	16.0	0.090	0.1736	7.2
0.0937	0.0062	3.25	0.049	0.2187	6.4
0.0969	0.0031	1.50	0.045	0.2376	5.6
0.0984	0.0016	1.19	0.048	0.2558	5.3
0.0992	0.0008	1.09	0.044	0.2614	5.1

strength of these observations Miller says: "The fact that the concentration of sulfate (or oxalate) in the solution divided by its concentration in the precipitate, expressed as molecular percent of the sulfate plus the oxalate concentration, yields a constant, indicates that the precipitate is behaving as a single solid phase—a solid solution." It is difficult to see how Miller arrived at this conclusion since it is not verified or even suggested by his own data, the maximum value for the alleged constant for sulfate being over a thousand times, and for oxalate more than ten times its minimum value. Even if these values had been constant, the data would not have justified the above conclusion since the hydrogen ion concentration was allowed to vary through wide limits and this is the determining factor in the particular range of variation that Miller happened to get. It should be noted further, that as the ratio of total sulfate to oxalate falls off the value for the sulfate constant increases, the increase being very rapid as equal concentrations of sulfate and oxalate are approached. Had Miller taken ratios of oxalate to sulfate greater than one, the so-called constant for sulfate would have been found to approach infinity very rapidly, for from a neutral solution the adsorption of sulfate becomes zero in the presence of an appreciable excess of oxalate. This is illustrated by some comparable observations on the simultaneous adsorption of sulfate and oxalate by hydrous chromic oxide, recorded in Table VIII. In these observations the adsorption of 25 cc of the N/50 solution corresponds to 1.77 milli-equivalents per gram of chromic oxide. Since the precipitation concentrations as well as the adsorptions of oxalate and sulfate are so nearly equal, one might be led to conclude that their adsorptions would be nearly

equal when both are present in the same solution. This is not even approximately true if the solution is neutral or basic. In order to get any measurable quantity of sulfate adsorbed at pH of 8 it is necessary to have a very low concentration of oxalate, and to get equivalent adsorptions at this pH value the final concentration of sulfate must be approximately 128 times that of oxalate. The conclusions to be drawn from these data are: First, under the same conditions the equivalent adsorption by the hydrous chromic oxide is approximately equal whether it be all sulfate, all oxalate, or some of each. Second, so long as there is an excess of oxalate in the bath it displaces the sulfate almost completely while an excess of sulfate has but little effect on the

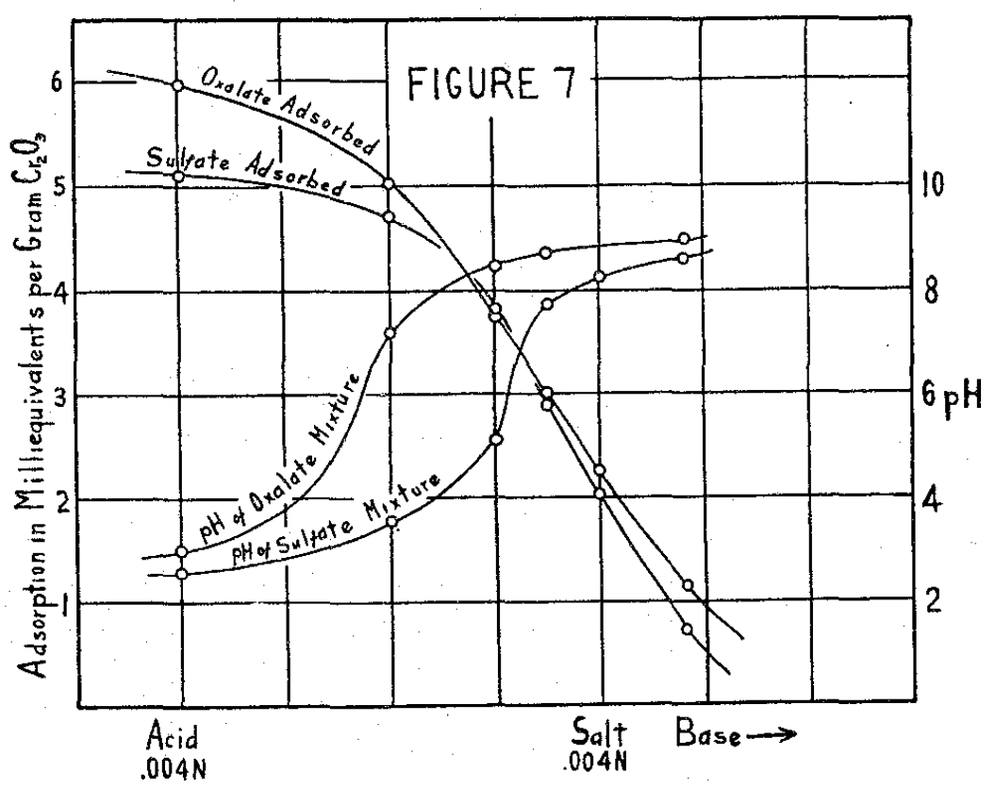


TABLE VIII

Adsorption by Hydrous Chromic Oxide from Mixtures of Oxalate and Sulfate

Cc of soln. mixed with 50 cc of sol containing 0.283 grams of Cr_2O_3 in a total of 150 cc		Adsorption in milli-equiv. per gram of Cr_2O_3			pH values after adsorption
N/50 $K_2C_2O_4$	N/50 K_2SO_4	oxalate	sulfate	total	
50	0	2.13	0.0	2.13	8.30
60	0	2.17	0.0	2.17	8.37
50	25	2.09	−0.03	2.06	
50	50	2.04	0.14	2.18	8.11
25	50	1.45	0.46	1.90	7.68
10	50	0.65	1.30	1.95	7.49
0	50	0.00	1.86	1.86	7.32
25	25	1.63	0.36	1.99	7.97

adsorption of oxalate. Third, it is necessary to limit the concentration of the oxalate in order to make a study of the simultaneous adsorptions of oxalate and sulfate in a neutral or basic solution.

To determine the effect of varying hydrogen ion concentration in the simultaneous adsorption, a total quantity of oxalate plus sulfate corresponding to 6.2 milliequivalents per gram of oxide was used throughout the series of observations. In actual quantities of reagents, this is represented by sufficient sol to contain 0.125 grams of oxide and 40 cc of the N/50 solutions. The relative concentrations were varied as follows: In series one were used, 40 cc of the sulfate solutions, in series two, 40 cc of the oxalate solutions, in series three, 20 cc of each, in series four, 30 cc of sulfate and 10 cc of oxalate, and in series five, 35 cc of sulfate and 5 cc of oxalate. The observations of series one, two, and three are recorded in Table IX. The data of series one and two are shown graphically in Fig. 7 and the data of series three in Fig. 8. The data of series four and five are not included in this paper since they are in entire agreement and furnish no additional information.

TABLE IX

Adsorption by Hydrous Chromic Oxide from Mixtures of Oxalate and Sulfate at varying pH Values

Cc of soln. mixed with 50 cc of sol containing 0.125 grams of Cr_2O_3 in a total of 200 cc					Adsorption in milli-equiv. per gram of Cr_2O_3			pH values after adsorption
N/50 $K_2C_2O_4$	N/50 $H_2C_2O_4$	N/50 K_2SO_4	N/50 H_2SO_4	0.037 N KOH	oxalate	sulfate	total	
0	0	0	40	0	0.0	5.08	5.08	2.53
0	0	20	20	0	0.0	4.71	4.71	3.56
0	0	30	10	0	0.0	3.77	3.77	5.12
0	0	35	5	0	0.0	2.87	2.87	7.76
0	0	40	0	0	0.0	2.03	2.03	8.27
0	0	40	0	2	0.0	1.53	1.53	8.42
0	0	40	0	5	0.0	0.71	0.71	8.62
0	40	0	0	0	5.96	0.0	5.96	3.05
20	20	0	0	0	5.02	0.0	5.02	7.20
30	10	0	0	0	3.75	0.0	3.75	8.43
35	5	0	0	0	3.02	0.0	3.02	8.73
40	0	0	0	0	2.26	0.0	2.26	——
40	0	0	0	5	1.13	0.0	1.13	8.97
0	20	0	20	0	2.97	2.65	5.62	3.03
20	0	0	20	0	2.95	1.92	4.87	4.20
20	0	10	10	0	2.83	0.73	3.56	7.49
20	0	15	5	0	2.50	0.32	2.82	7.94
20	0	20	0	0	2.02	0.13	2.15	8.02
20	0	20	0	5	1.00	0.00	1.00	8.91

As the adsorption increases with the hydrogen ion concentration, it will be noted that there is little or no adsorption of the sulfate from the mixture until the oxalate in the bath is nearly exhausted, after which there is a marked increase in sulfate adsorption as shown by the sharp rise in the adsorption curve. The curves for the separate adsorptions of the ions serve as a check on those in Figs. 1 and 3. It is interesting to note that the sum of the simultaneous oxalate and sulfate adsorptions approximate a mean between their separate adsorptions at the hydrogen ion concentrations investigated. This is not in accord with the general conclusion of Mehrotra and Sen to which reference has been made.

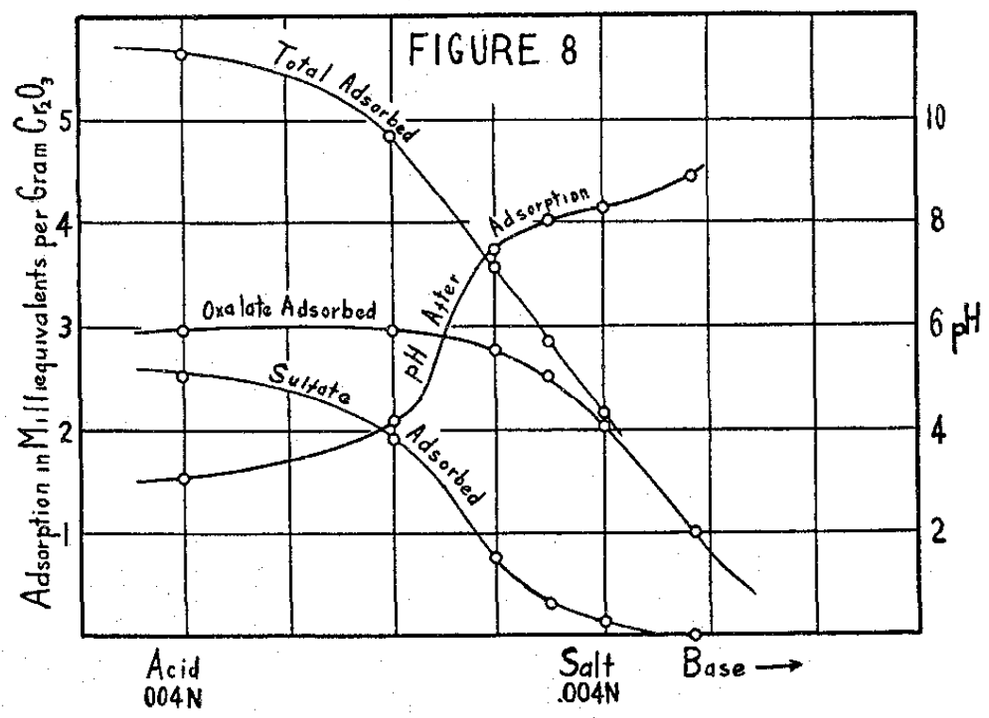
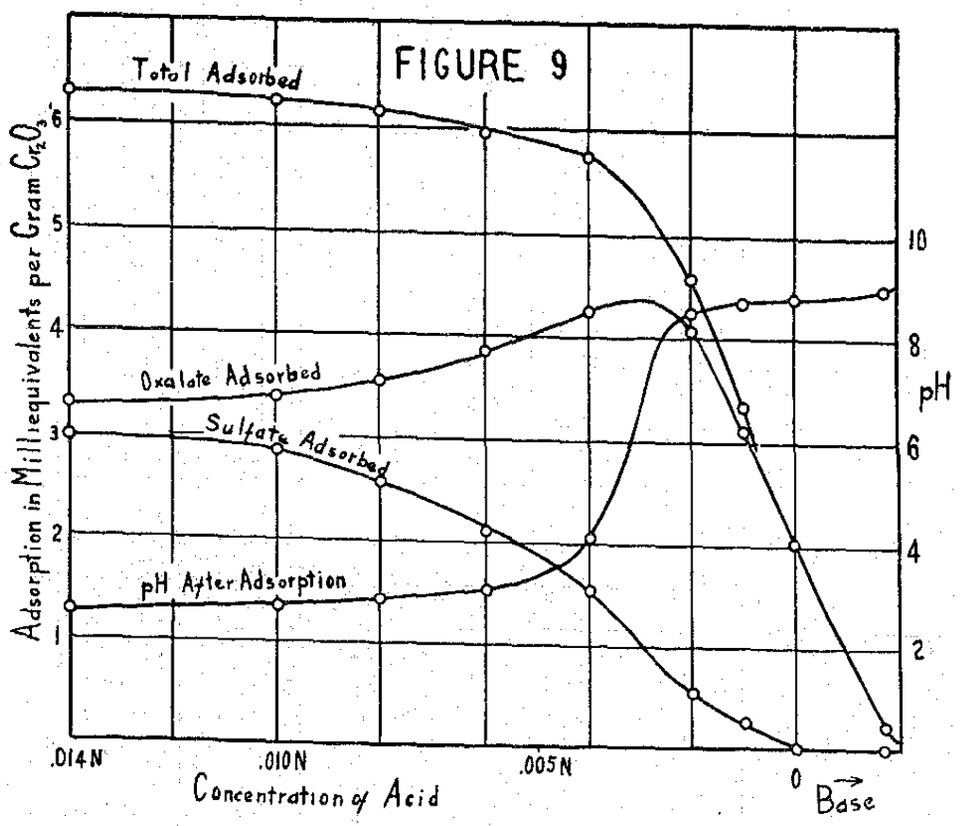


TABLE X

Replacement of Oxalate by Sulfate at low pH Values

Cc of soln. mixed with 50 cc of sol containing 0.125 grams of Cr_2O_3 in a total of 200 cc						Adsorption in milli-equiv. per gram of Cr_2O_3			pH values after adsorption
0.037 N KOH	N/50 K_2SO_4	N/50 H_2SO_4	N/50 $K_2C_2O_4$	N/50 $H_2C_2O_4$	N/25 HCl	oxalate	sulfate	total	
10	50	0	50	0	0	0.23	0.01	0.22	8.91
0	50	0	50	0	0	2.01	0.01	2.00	8.80
0	40	10	50	0	0	3.12	0.25	3.37	8.68
0	30	20	50	0	0	4.04	0.53	4.57	8.51
0	10	40	50	0	0	4.25	1.54	5.79	4.06
0	0	50	40	10	0	3.81	2.09	5.90	3.06
0	0	50	20	30	0	3.56	2.56	6.12	2.85
0	0	50	0	50	0	3.37	2.85	6.22	2.72
0	0	50	0	50	20	3.31	2.96	6.27	2.59

Since, with increasing hydrogen ion concentration the adsorption of sulfate increases more rapidly than that of oxalate when the oxalate concentration is relatively low, it seemed likely that if the hydrogen ion concentration were sufficiently great, the adsorption might show a similar shift even in the presence of an excess of oxalate. This was confirmed in a striking manner as shown by the data of Table X and Fig. 9. In the experiments, the total concentration of the oxalate and sulfate were each equal to 0.005 normal throughout. This concentration is sufficiently high so that at maximum adsorption the bath will not be exhausted with respect to either ion. The form



of the adsorption curves show: first, that the oxalate is displaced appreciably by the sulfate when the final solution is but faintly acid; and second, that the adsorptions approach equivalence in the strongly acid solution. This observed behavior is probably not due to a shift in the relative adsorbability of the bivalent oxalate and sulfate ions but is due to the relatively greater conversion of bivalent oxalate to the less strongly adsorbed bioxalate ion than of the bivalent sulfate to bisulfate ion in the acid solution. In the paper on alizarin lakes it will be shown that the behavior of oxalate in this respect is typical of the acid dyes.

Summary

1. Preliminary to the study of the mechanism of color lake formation, investigations were carried out to determine the effect of hydrogen ion concentration on the adsorption of an inorganic anion, sulfate, and an organic anion, oxalate, both separately and simultaneously by the hydrous oxides of chromium, aluminum, and iron which are the most common metallic mordants

or color bases. Observations were also made on the effect of calcium ion on the adsorption of anions by the hydrous oxides at constant hydrogen ion concentration.

2. Increasing the concentration of hydrogen ion raises the charge on the particles of hydrous oxides, thereby increasing their capacity to adsorb anions. The adsorption of the latter falls off quite rapidly on the alkaline side of the neutral point, being completely nullified at a pH value of about 9.2. However, both hydroxyl and sulfate or oxalate are adsorbed in the alkaline range. In Loeb's investigations on the proteins it seems probable that the specific effects of cations other than hydrogen and of anions other than hydroxyl were overlooked since he worked with relatively low concentrations of salts.

3. A study of the simultaneous adsorption of sulfate and oxalate discloses the fact that the former is adsorbed much more strongly than the latter in the alkaline and neutral range. From the basic solution no measurable quantity of sulfate is adsorbed in the presence of an excess of oxalate. From a neutral solution, the adsorption of sulfate and oxalate are equal when the ratio of the sulfate to the oxalate concentration is about 128 to 1. This ratio falls off rapidly in an acid solution, having a value of 1.1 to 1 at a pH value of 2.5.

4. Miller's conclusion that the taking up of anions by hydrous oxide gels is a solid solution phenomenon has been disproven.

5. The sum of the simultaneous adsorptions of sulfate and oxalate approaches a mean between their separate adsorptions at the same hydrogen ion concentration. This is not in accord with Mehrotra and Sen's conclusion that the sum of the adsorptions of two ions from a mixture is always greater than the adsorption of either of them present alone in the solution.

6. The relationship between the hydrogen ion concentration and the precipitation concentrations of sulfate and oxalate has been investigated. The precipitation concentration of sulfate is greater than that of oxalate in the neutral solution but, owing to the formation of bioxalate ion, a slight increase in the hydrogen ion concentration reverses the order, although when expressed as equivalents the adsorption of oxalate is greater than that of sulfate even at pH values as low as 2.5. The discrepancy is accounted for by the fact that some bioxalate is actually adsorbed and figured as if it were bivalent oxalate.

7. It was observed previously that the precipitation concentration of potassium sulfate was less than that of potassium oxalate for a Crum's alumina sol although the adsorption of oxalate by the precipitated gel was greater than that of sulfate. Since the sol employed was acid this anomalous behavior is now explained.

8. Since both hydrogen and hydroxyl ions are adsorbed very strongly by the hydrous oxides, any conclusions based on precipitation or adsorption data obtained with hydrous oxides are of questionable value unless the observations are made at the same hydrogen ion concentration. Varying the hydrogen ion concentration may also have a marked effect on the substance adsorbed.

Department of Chemistry,
The Rice Institute,
Houston, Texas.

THE SIGNIFICANCE OF ISO-CATALYTIC DATA AND THE SO-CALLED PROTION THEORY OF CHEMICAL REACTIVITY

BY HARRY MEDFORTH DAWSON

In a recent paper, Bergstein and Kilpatrick[1] discuss the investigations of Dawson and Powis[2] on the nature of the autocatalysed reaction which takes place when iodine is added to an aqueous solution of acetone and ascribe to these authors a method of interpreting their experimental results which is obviously based on a misconception of the actual facts. In these experiments, Dawson and Powis measured the rate of disappearance of the iodine, and found that the connection between the fall in the iodine concentration (x) and the time (t) was in very close agreement with that calculated on the assumption that the reaction proceeds in accordance with the equation

$$dx/dt = kx$$

the integration of which shows that log. x is a linear function of *t*.

Since the hydriodic acid which is produced could be regarded as almost completely ionised, it appeared that the progress of the reaction in the measurable stage was determined by the concentration of the hydrogen ion. On the assumption that the relations in the early stages of the reaction were the same as for the later measurable stage, extrapolation to t = o gave a value of *x* which it was suggested might be taken as a measure of the apparent initial hydrogen ion concentration. This apparent initial hydrogen ion concentration was found to be unaffected by the addition of small amounts of alkali, but was diminished by the addition of small quantities of a strong acid.

In referring to the above experiments, Bergstein and Kilpatrick assert that the interpretation of the observations was based on the use of the equation

$$dx/dt = k(c + x)$$

in which *c* is the initial hydrogen ion concentration and *x* the concentration of the hydrogen ion produced by the chemical change. This equation conflicts so completely with the elementary principles which are involved in the consideration of the influence of strong acids on the hydrogen ion concentration of solutions of weak acids, that it is necessary to point out that Dawson and Powis did not make use of this equation. Although they were unable in 1912 to offer a complete explanation of the observed results, they recognised that if the apparent initial hydrogen ion concentration had any real significance, its origin was such that its value would be greatly reduced by the autocatalytically generated hydrogen ion. This view obviously precluded the possibility of the use of a formula according to which the total hydrogen ion concentration is represented by the sum of the concentrations of the hydrogen ion initially present and of the hydrogen ion produced by the reaction.

[1] J. Phys. Chem., **30**, 1616 (1926).
[2] J. Chem. Soc., **101**, 1502 (1912).

Although the equation $dx/dt = k(c + x)$ is unacceptable, an equation of this type has actually been used by Bergstein and Kilpatrick as the starting point for the further consideration of the early stages of the auto-catalysed reaction in which the catalytic activity of the hydroxyl ion is taken into account. In view of the circumstances that the basic equation is incorrect, the considerations which they put forward are unsound.

The problem of the auto-catalysed reaction in which catalytic effects ar- attributable to the hydrogen and hydroxyl ions has been dealt with in a come prehensive manner in a recent paper[1] by the writer with special reference to the acetone-iodine reaction. The conclusions reached are very different from those drawn by Bergstein and Kilpatrick. These authors assert that the activity of the hydroxyl ion is so great that the condition of minimum velocity is reached almost instantaneously and that the ratio of the initial hydrogen ion concentration $[H^+]_o$ to the hydrogen ion concentration $[H]_i$ at the iso-catalytic (minimum velocity) point is given by $[H^+]_o = \sqrt{2}[H^+]_i$. In marked contrast with these conclusions, the writer has shown that the catalytic activity of the hydroxyl ion is about 40,000 times as great as that of the hydrogen ion, that when the concentration of the acetone is 20 cc. per litre, the time required at 25° for the attainment of minimum velocity is about twelve hours, and, further, that the apparent initial hydrogen ion concentration is really a measure of the hydrogen ion concentration at the iso-catalytic point.

The stage of the reaction at which the velocity has its minimum value corresponds with such a very small fall in the iodine concentration (2×10^{-5} mols. per litre), that the direct observation of minimum velocity in the simple autocatalytic change is impossible. Experiments now in progress under somewhat modified conditions afford, however, a direct proof of the reality of the iso-catalytic point in the auto-catalysed reaction and serve to confirm quantitatively the accuracy of the writer's previous conclusions.

The results obtained in the study of such auto-catalysed processes are in accord with the general theory of acid catalytic effects which has been described in a series of papers[2] published from this laboratory. The investigation of acid and salt effects in catalysed reactions has indeed shown that catalytic activity must be attributed to the hydrogen ion, to the acid anions and to the undissociated acid molecules. In accordance with this, the observed velocity of reaction is to be represented as the sum of effects which, in the case of an aqueous solution of an acid HA, may be expressed by

$$v = v_h + v_a + v_{OH} + v_m + v_w$$
$$= k_h[H^+] + k_a[A^-] + k_{OH}[OH^-] + k_m[HA] + k_w[H_2O] \qquad (1)$$

If a comparison is made of the reaction velocities for a group of solutions represented by the general formula cHA + xMA where c is constant and x is variable, then since

[1] J. Chem. Soc., **1927**, 458.

[2] Dawson and Carter: J. Chem. Soc., **1926**, 2282; Dawson and Dean: 2872; Dawson and Hoskins: 3166; Dawson: **1927**, 213; Dawson and Hoskins: Proc. Leeds Phil. Soc., **1**, 108 (1926).

$$[H^+] \cdot [A^-] = K\,[HA] \text{ and } [H^+]\,[OH^-] = K_w$$

it is possible to eliminate $[A^-]$ and $[OH^-]$ from the above equation which then assumes the form

$$v = (k_h - k_m)\,[H^+] + (k_a Kc + k_{OH}\,K_w) / [H^+] + k_m\,c + k_w c_w \qquad (2)$$

By differentiation, it may be shown that the reaction velocity passes through a minimum value when the concentration of the hydrogen ion has the value given by

$$[H^+] = [H^+]_i = \sqrt{(k_a Kc + k_{OH}\,K_w) / (k_h - k_m)} \qquad (3)$$

By substitution of this value of $[H^+]$ in the previous equation, it is found that the minimum reaction velocity is given by

$$v_i = 2\sqrt{(k_h - k_m)\,(k_a Kc + k_{OH} \cdot K_w)} + k_m c + k_w c_w \qquad (4)$$

If the reaction velocity characteristic of the above group of solutions is plotted against the logarithm of the hydrogen ion concentration, or against pH, a symmetrical curve of catenary type is obtained, which has been termed the catalytic catenary. For each value of *c* there will be a corresponding catenary and the catalytic effects produced by all possible mixtures of the acid HA, with the corresponding salt MA, can thus be represented by a continuous series of catalytic catenaries the combination of which gives rise to a catenary surface in space defined by the coordinates *v*, pH and *c*.

The catenary surface is limited in the direction of the *c* coordinate by the catenary which corresponds with $c = 0$. This limiting catenary is the $H^+ - OH^-$ catenary which represents the catalytic effects which are jointly due to the hydrogen and hydroxyl ions. The hydrogen ion concentration for which the reaction velocity has a minimum value is under these circumstances given by

$$[H^+]_i = \sqrt{k_{OH} \cdot K_w / k_h} \qquad (5)$$

On the other hand, when the concentration of the acid HA is so large that the catalytic effect of the hydroxyl ion may be left out of account, the hydrogen ion concentration for minimum reaction velocity is given by

$$[H^+]_i = \sqrt{k_a K_c / (k_h - k_m)} \qquad (6)$$

Between this group of $H^+ - A^-$ catenaries and the $H^+ - OH^-$ catenary, there is a continuous series of compound catenaries characterised by the circumstance that the catalytic effects due to the negative ions are shared by the acid anion and by the hydroxyl ion. For such compound catenaries, the hydrogen ion concentration corresponding with minimum reaction velocity is given by equation (3).

The relations referred to in the preceding paragraphs represent certain important features of the general theory of catalytic effects in acid catalysed reactions which have been described in the various papers previously referred to. They are in close agreement with the experimental results which have been established by the detailed study of the catalytic effects of acid-salt mixtures in the acetone-iodine reaction and may be regarded as entirely contrary to the requirements of the protion theory of chemical reactivity advanced by Rice.[1] According to this theory, the velocity of hydrolytic re-

[1] J. Am. Chem. Soc., **45**, 28c8 (1923).

actions, i.e., of reactions which are catalysed by both the hydrogen and hydroxyl ions, should have a minimum value at about pH = 5. This is certainly far from the truth. On the contrary, since the hydrogen ion concentration at the point of minimum velocity is given by equation (5) its value at a given temperature, and therefore at a fixed value of K_w, is determined by the ratio of the velocity coefficients k_{OH} and k_h. According to the nature of the reaction, the value of k_{OH}/k_h varies very widely. Actual observations show that a variation in the ratio from 1 to 1,000,000 is by no means extreme. Such a variation would correspond with a change in the value of $[H^+]_i$ represented by 1 : 1,000, and with a difference in the pH value of the isocatalytic point of 3 units. Such variations in the pH value of the point of minimum velocity of hydrolytic reactions are obviously in complete disagreement with the so-called protion theory.

In this connection it may be pointed out that reactions, which are catalytically accelerated by hydrogen and hydroxyl ions, are in general affected similarly by other acid ions. The investigation of the effects produced by the joint action of the hydrogen and acetic ions in the acetone-iodine reaction has shown that the point at which minimum reaction velocity is attained in the case of acid-salt mixtures of constant acid concentration varies from pH = 4.33 for 0.01 N acetic acid to pH = 3.23 in the case of 1 N acetic acid. For acid concentrations between 0.01 N and 0.50 N the observed pH values are in very close agreement with those calculated from equation (8). For solutions which contain acetic acid in 1 N concentration, the observed catalytic effects appear to be somewhat complicated by the formation of complex acetate ions.

In contradistinction to the requirements of the protion theory, it may therefore be asserted that the pH value which corresponds with the minimum catalytic effect of a given pair of ions, is determined by the velocity coefficients k_h, k_a, and k_m and by the ionisation constant and the concentration of the acid from which the catalytically active entities are derived.

Summary

I. The interpretation of observations on the autocatalytic reaction between acetone and iodine is discussed.

II. The factors which determine the incidence of minimum reaction velocity are considered in relation to the catalytic catenary, and it is shown that the protion theory of chemical reactivity is entirely inconsistent with established facts.

Physical Chemistry Department
The University
Leeds.
March 25, 1897.

SOME ELECTROCHEMICAL STUDIES OF TITANIUM*

BY ELBERT D. BOTTS AND FRANCIS C. KRAUSKOPF

Introduction

Investigations have shown that certain elements, distinctly non-metallic in nature, have the property of replacing metals from aqueous solutions of their salts. For example, phosphorus will replace copper from solutions of copper sulfate, the phosphorous ultimately appearing in the solution as acids of phosphorus.[1] W. R. Mott[2] worked out a quantitative method for the determination of elemental silicon in the presence of silica, iron oxide, etc., basing the method upon the fact that silicon will replace an equivalent quantity of silver from a solution of silver fluoride. No replacement with silicon takes place in solution of salts other than fluorides.

Gilbert[3] attempted to determine the single potential of silicon and correlate this with its ability to replace silver and copper from solutions of their salts. He found it quite difficult to obtain consistent results because of the peculiar tendency of silicon to polarize and to show decided changes in potential with any variation in treatment preceding its use as an electrode.

On account of hydrolysis it is practically impossible to prepare a solution such that single potential measurements of silicon can be made against positive silicon ions. It was thought, therefore, that titanium, being a chemical analogue of silicon, would serve the purpose to better advantage since well-defined salts of trivalent titanium are known which are not as completely hydrolyzed as those of silicon.

Metallic titanium has been prepared in a number of ways and many of its properties have been investigated. Its specific heat, density, and melting point have been determined by several investigators, but the literature contains no record of any attempt to measure its single potential. Also, the conditions for its preparation in the pure state have not been described with sufficient clearness to permit easy duplication.

The objects of this investigation were:

(1) To study further the preparation of metallic titanium;

(2) To determine the single potential of titanium and its ability to replace metals from solutions of their salts.

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*Contributed from the Laboratory of General Chemistry of the University of Wisconsin.

**This material is taken from the thesis of Mr. E. D. Botts, presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

[1] Bird and Diggs: J. Am. Chem. Soc., 36, 1382 (1914).

[2] Mott: Electrochem. Met. Ind., 5, 455 (1907).

[3] Gilbert: B. A. Thesis, U. of Wis., (1915).

Part I. Preparation of Metallic Titanium

Wöhler prepared titanium metal from its compounds by the reduction of the alkaline fluotitanate with sodium, in a current of hydrogen.[1] Schneider showed that the metal obtained in this way is impure, containing among other things considerable hydrogen.[2]

Moissan made an advance when he reduced the anhydride of titanic acid in the electric furnace with carbon.[3] He obtained a product which was about 97% pure, containing however, considerable carbon which probably affected the individual properties of titanium to a great extent.

Aluminum has been tried as in the Goldschmidt process but has produced only alloys.[4]

Hydrogen has also been employed to reduce the tetrachloride using temperatures up to 1100° C., but the resulting amorphous powder contained but 94% to 95% titanium.

The best method that has been recorded up to the present time seems to be that of Nilson and Pettersson,[5] in which they reduced titanium tetrachloride with sodium in a steel bomb. They obtained a product of about 95% purity.

Many years later, Hunter[6] improved the method and obtained thereby a product which, in some cases, analyzed as high as 99.9% titanium. He was able to produce rather large quantities and has described various physical properties of the metal. This method was adopted in the present research.

Billy[7] devised a very ingenious way of making small quantities of pure amorphous titanium. He reduced carefully purified $TiCl_4$ by sodium hydride and obtained a product of 100% purity.

Experimental.

The method originated by Nilson and Pettersson and improved by Hunter was chosen as the most desirable way in which titanium metal could be produced in pieces large enough for investigational work in electrode potentials.

The cylindrical bomb used for this purpose was of the highest grade chrome-vanadium steel, the outer diameter being 7.5 centimeters, and the inner diameter of the reaction chamber being 3.5 centimeters. The depth of the chamber was 16 centimeters and its capacity approximately 150 cubic centimeters. The top inner part of the bomb was threaded so it could serve as a nut for a heavy cap, fitting into the bomb and pressing upon the gasket which rested upon the shoulder at the top of the reaction chamber. This provision was not entirely satisfactory for holding all of the gases due to the pressure developed during the course of the reaction, but by cementing the gasket with a little litharge-glycerine mixture it was maintained entirely tight and held all gases developed.

[1] Wöhler: Ann., **73**, 34, 74, 212 (1849); Wöhler and Deville. Compt. rend., **45**, 480 (1857).
[3] Schneider: Z. anorg., Chem., **8**, 81 (1895).
[3] Moissan: Compt. rend., **120**, 290 (1895).
[4] Stavenhagen and Schuchard: Ber., **35**, 909 (1902).
[5] Nilson and Pettersson: Z. physik. Chem., **1**, 28 (1887).
[6] Hunter: J. Am. Chem. Soc., **32**, 330 (1910).
[7] Billy: Ann. Chimie, **16**, 1 (1921).

The $TiCl_4$ used in the preliminary investigation was the ordinary commercial product. Later in attempting to procure a purer product, the $TiCl_4$ was purified by the method recommended by Billy and then fractionally crystallized by immersing the container in liquid air. This process left a pure, perfectly water-clear product.

The sodium and potassium used were the ordinary Merck's C. P. The film which forms on the surface of the metal was always removed before using.

Pieces of sodium were placed in the bomb, and the $TiCl_4$ poured over them. The top of the bomb was carefully flushed with CO_2 and the cap screwed down under great pressure upon the gasket which had been covered with a thin coat of litharge-glycerine cement. In this condition the bomb was allowed to stand for about 24 hours to allow the litharge-glycerine seal to set. It was then placed in an electric coil furnace specially provided for it and the temperature of the entire system raised to a red heat after which it was cooled, opened, and the contents removed. The shape of the bomb made it difficult to remove the mass resulting from the reaction. The contents were solidly cemented together and very inaccessible to working tools. Alcohol was first added, followed by water, in order to destroy any free sodium that might have been left, and then by alternate chiseling and treatment with water, the contents were removed and mechanically separated.

In all these experiments, the necessity of obtaining an absolutely air-tight seal was very pronounced. If at any time during the heating process a leak developed the result was invariably a smaller yield and an inferior product with respect to the size of the pieces of titanium. Another important factor which may have been due to the individual peculiarity of the bomb, was the size of the pieces of sodium used. In the first experiments practically the entire amount of sodium used was in the form of one or two large pieces. In these cases a large quantity of free sodium remained at the end of the reaction and the yield of titanium was small. Sodium "shot" was then tried but it was also unsatisfactory. While the excess sodium was slight when the correct proportions were used, the titanium produced was either a very fine amorphous powder or in small pieces. For the next series of trials, the sodium was cut into cubes slightly less than one cubic centimeter in size. This condition, when the quantity was adjusted, was found to be most favorable for the production of suitably-sized pieces of titanium.

At first, it was assumed to be unnecessary to use equivalent molecular quantities of $TiCl_4$ and sodium but such was not the case for the bomb used in this work. The best product obtained was from those mixtures using less sodium than the 4 mols of sodium per mol of $TiCl_4$ as indicated in the reaction, $TiCl_4 + 4\ Na = Ti + 4\ NaCl$. A more suitable mixture was found to be 1 mol $TiCl_4$ to $3\frac{1}{2}$ mols of sodium. The bomb used having an approximate capacity of 150 cc. permitted the introduction of 50 grams of sodium and 75 cc. of $TiCl_4$ in such a manner that the cap could be screwed down tightly, leaving a slight space above the mixture. The air in this space was replaced by CO_2 and the bomb sealed and heated as previously described.

In all cases there was an excess of sodium left in the bomb, and a few times a little $TiCl_4$ was also present. When the larger pieces of sodium were used, a layer of sodium chloride formed around them and left an appreciable amount of the free sodium which often caused sharp explosions when the product was being washed out of the bomb. In almost every case $TiCl_3$ and $TiCl_2$ were present in the product though under the optimum conditions they were scarcely noticeable. The finely divided amorphous material obtained always contained TiO_2.

A study was made to determine whether or not other metals, such as potassium, aluminum, magnesium and mercury could be used to advantage in place of sodium. The ratio of 1 mol $TiCl_4$ to 3.5 potassium was tried several times. In other instances the amount of potassium was reduced, but under all conditions tried the product was the fine amorphous titanium mixed, as in the sodium experiments, with the lower chlorides and with free potassium. No beads or larger pieces of titanium were ever formed when potassium was used as the reducing agent. A mixture of sodium and potassium gave no better results.

It is probable that with the use of potassium and $TiCl_4$ reduction takes place at a much lower temperature and the reaction thereby fails to develop a temperature sufficient to melt the metallic titanium formed. It is quite evident that the masses of Ti formed in some cases in the sodium reduction of the tetrachloride have resulted from the development of an intense heat produced by the reaction. The melting point of titanium according to Hunter is approximately 1850° C. The temperature of the outer part of the bomb was at no time raised to more than 750° C. This would indicate that there was developed an intense local heat within the bomb, since in many cases large pieces of the metallic titanium were produced in such form as would prove them to be the result of cooled fusion. When the other metals were used some reduction occurred but no metallic titanium resulted. It thus seems evident that sodium is the most suitable reducing agent to use in preparing titanium by this method.

In three typical runs in each of which 75 cc. of $TiCl_4$ and 50 grams of sodium were used, there were obtained approximately 18, 15 and 14 grams of crystalline titanium, and about 8, 10 and $10\frac{1}{2}$ grams of amorphous titanium powder respectively. It was obviously impossible to give more than a rough estimate of the amount of amorphous titanium formed, because in removing it from the bomb it always became contaminated with TiO_2.

The purity of the pieces of crystalline titanium obtained in this manner showed a considerable degree of variability. In the first trials in which conditions were being adjusted the purity was low, due in part, undoubtedly, to the impure $TiCl_4$.

The analysis of various pieces was effected by dissolving the metal in a mixture of HF and H_2SO_4 in which H_2SO_4 predominated. This solution was diluted, the titanium precipitated with ammonium hydroxide, filtered, ignited and weighed as TiO_2.

The results of some typical analyses are given in Table I.

TABLE I

Analyses of Different Samples of Titanium

No. of run	Wgt. of Ti taken grams.	Wgt. of TiO_2 found grams.	% Ti.
1	0.1900	0.3039	96.2
3	0.3964	0.6318	96.5
8	0.3921	0.6500	99.4
9	0.2432	0.3948	97.1

One piece of the metallic titanium weighing about 2 grams was found, which on three samples chipped from various parts of the piece showed the following percentages of titanium: 99.7%; 99.6%; 99.9%. This piece was used in the more exact single potential measurements.

Part II. Single Electrode Potential of Titanium

Apparatus and Materials.

The apparatus used for these determinations consisted of a Leeds and Northrup student potentiometer and resistance box, and an ordinary D'Arsonval galvanometer. The potentiometer measured voltage direct to three decimal places and permitted estimation to the fourth, but since for other reasons great accuracy could not be attained in this work, readings were not taken in the fourth place. The standards consisted of two Weston cells which had been standardized against a Bureau of Standards cell and which checked with each other.

The measurements recorded were made at room temperature which did not vary more than two degrees from 25° C. at the time of any measurement. This change of temperature did not affect the degree of accuracy which was sought in this work.

The titanium tetrachloride used for the preparation of the trivalent titanium compounds was purified as outlined in the first part of this paper, viz., aeration, standing over sodium amalgam and distillation. The trichloride was prepared by cathode reduction of the purified tetrachloride solution.[1] The trivalent sulfate was prepared by heating the trichloride and a dilute solution of sulfuric acid at a low pressure till the separation of 3 $Ti_2(SO_4)_3$. $H_2SO_4 \cdot 25H_2O$ took place. This was washed with ether and heated under reduced pressure to 190° – 200° C. whence resulted $Ti_2(SO_4)_3$ a grayish green powder.

Experimental.

A few qualitative experiments using titanium as one electrode in various electrolytes indicated the difficulties that would be encountered in trying to get an exact measurement of the single electrode potential. The treatment of the titanium electrode previous to its introduction into a cell had a marked influence on its behavior in the cell and on the value of the sinlge potential given. Polishing with sand paper, for example, might even change it temporarily several tenths of a volt. By giving it the same treatment each time

[1] Polidori: Z. anorg. Chem., 19, 306 (1899).

before introducing it into a new cell, fairly concordant results could be obtained and it was hoped that an indication of its general location in the electromotive series could be inferred.

In the following experiments which are qualitative only, the titanium used was a large piece of at least 97% purity. It was attached securely to a platinum wire for the outside circuit and the contact points covered with wax. This portion was not allowed to dip into the electrolyte. Adopting for all of the following work the convention used by Lewis and Randall,[2] the cells are represented in such a manner that negative electricity will flow through the cell from right to left. Thus the cell, consisting of zinc and copper in sulfuric acid, would be represented

$$Zn - H_2SO_4 - Cu.$$

In such a cell the zinc is represented as being more active, hence should replace copper from solutions of its salts. (N.E as used throughout the following pages carries the usual significance of normal calomel electrode.) The results obtained are shown in Table II.

TABLE II

Titanium Electrode compared with Other Electrodes

Exp. No.	Cell	E. M. F.
1	Cd $N/_1$ H_2SO_4 Ti	.872
2	N.E. NH_4NO_3 (sat. sol.)$N/^1CuSO_4$, Ti	.165
3	N.E. NH_4NO_3 (sat. sol.)$N/^1H_2SO_4$, Ti	.113
4	Cu $N/_1H_2SO_4$ Ti	.111
5	Ti $N/_1H_2SO_4$ (containing HF), Cu	.785

In the above measurements which are at best only qualitative, constancy of E. M. F. was very hard to obtain. It will be seen here that titanium in the ordinary cell seems to be even below hydrogen in activity. In a solution containing hydrofluoric acid, the electrodes are reversed in sign and the voltage raised enormously. However, the measuremnt of a potential difference of a metal against the ions of another element may not mean a great deal, so far as the normal action of the electrode is concerned. Hence it was decided to try titanium solutions where the E.M.F. of the single electrode would be measured against titanium ions in solution, or in other words, would become a function of the osmotic pressure of titanium ions and of the solution pressure of the solid metal.

Obviously, it would not be worth while to measure the potential against the tetravalent ion since solutions of these ions always contain free acid and the titanic salts are reduced by titanium according to the equation

$$3\ TiCl_4 + Ti = 4\ TiCl_3$$

This is a case entirely analogous to the study of the potential of iron in Fe" and Fe"' solutions as described by Richards and Behr,[3] in which they main-

[1] Stähler: Ber., 38, 2621 (1905).
[2] Lewis and Randall: "Thermodynamics," 390 (1923).
[3] Richards and Behr: Z. physik. Chem., 58, 301 (1907).

tain the futility of attempting to measure the potential of iron in ferric solutions. For this reason, the trichloride was prepared as previously described and used in making measurement of titanium single electrode potential. Two reference electrodes were made for this purpose, one a tenth-normal calomel and the other a normal calomel. The tenth-normal was checked against cadmium in the normal sulfate solution and against zinc in its normal sulfate solution. The cadmium arranged in the cell

$$Cd\ N/2\ CdSO_4\ \ KCl\ (sat.)\ \ 1\ N.E. = .737\ volts,$$

or, adopting hydrogen as zero and the tenth normal electrode as $-.336$, the cadmium single electrode potential was .401. The usual value is .398.

The cell

$$Zn\ m/2\ Zn\ SO_4\ \ KCl\ (sat.)\ .1\ N.E. = 1.089\ volts$$

and the zinc single potential was therefore .753. The correct value according to Lewis is .758.

The cell

$$Hg\ HgCl\ N\ KCl\ (sat.) - .1\ N\ KCl,\ HgCl\ Hg = .059\ volts$$

It will thus be seen that either of these electrodes was sufficiently accurate for this work.

Since even the titanous salts show a marked hydrolysis it was considered essential to have an excess of acid in the solution. In most cases, small concentrations of acid do not much affect the single potential. It was found in this case to exert a considerable effect, and instead of causing an increase in the single potential as would be expected, there was a decided decrease. Richards and Boyer[1] found a similar phenomenon in the case of gallium in gallium sulfate.

This behavior toward acid led to the question of whether or not the metal was serving as a hydrogen electrode. The electrode consisted of a small piece of the titanium, analyzing 99.9% pure, which was held securely by a platinum loop. It was found that no change of potential resulted, whether or not the platinum was exposed to the electrolyte. This proved that whatever the single potential value might be it was due to the titanium. As further evidence that it was not a hydrogen electrode, it was compared with a platinized platinum hydrogen electrode, and the titanium was used with hydrogen bubbling over it. This latter procedure produced no change in the potential of the titanium, but there was a wide difference in the E.M.F. of the Ti, H_2 cell and the Pt, H_2 cell.

A solution containing 16 grams of trivalent titanium per liter showed in the cell

$$Ti,\ Ti_2\ (SO_4)_3\ \ KCl\ (sat.)\ .1\ N.E.\ an\ E.\ M.\ F.\ of\ .460$$

Substituting the hydrogen electrode of platinum H_2 for the titanium an E.M.F. of .390 was developed. This is not conclusive evidence of course, but another experiment apparently shows conclusively that the titanium was not acting as a hydrogen electrode. An electrolyte, consisting of dilute sulfuric acid was used in the cell,

[1] Richards and Boyer: J. Am. Chem. Soc., 43, 274 (1921).

.1 N.E. KCl (sat.) H_2SO_4 Ti.

This cell showed an E.M.F. of .200 volt. Substituting the platinized platinum hydrogen electrode for the titanium the cell became:

Pt, H_2 H_2SO_4 KCl (sat.) .1 N.E.

and showed an E.M.F. of .427. Now upon the addition of just enough $Ti_2(SO_4)_3$ to the sulfuric acid to produce a faint violet color the latter cell became

Pt H_2SO_4 — KCl (sat.) .1 N.E.

and showed an E.M.F. of .424—three millivolts change—but the former cell on the addition of the $Ti_2(SO_4)_3$ became

Ti H_2SO_4 $Ti_2(SO_4)_3$ KCl (sat.) .1 N.E.

and had an E.M.F. of .472, a change of .67 volts. Similar experiments with hydrochloric acid and $TiCl_3$ gave similar results, and while the values given above may not be exactly reproducible, results of the same order always obtain.

It would seem, then, that although free acid affects a cell in which titanium is an electrode, the electrode is not acting as a hydrogen electrode. This is further confirmed by the fact that a little HF added to a solution strongly acid with HCl or H_2SO_4 will increase the single electrode potential of titanium enormously.

Upon being confronted with this set of conditons, it was decided to make the measurement of the single electrode potential in solutions freshly prepared from the pure $Ti_2(SO_4)_3$ and $TiCl_3$ salts. The $Ti_2(SO_4)_3$ was prepared as previously described and the $TiCl_3$ was precipitated as a hydrated salt from its acid solution by excess of HCl gas. The light violet crystals so produced were washed with ether, dried under reduced pressure of CO_2 and dissolved in previously boiled water the reducing value determined by standard ferric chloride solution, and a definite concentration of the $TiCl_3$ made up on this basis. All of these operations were carried out in an atmosphere of CO_2. The standard titanous solution was then placed in an ordinary half-cell connected to the intermediary saturated KCl by a tube provided with a stop cock. The titanium electrode was attached to a platinum wire which was sealed into a glass tube filled with mercury. This tube was fixed in a rubber stopper and closed the half-cell when the titanium was introduced into the solution contained in the cell. By means of the mercury contacts the cell

Ti — titanous salt, KCl (sat.), .1 N.E.

was connected to the potentiometer which was set up in the usual way. Readings could be taken from time to time very rapidly.

Accurate comparison of the effects of ion concentration can hardly be made, since the ion concentration of the titanous salts has not been determined. The substances are considerably hydrolyzed, possibly enough to reduce the titanium ion appreciably in dilute solution, forming a colloidal hydroxide. This tendency to hydrolyze becomes very apparent after the solution has stood a long time, some slight separation and precipitation eventually taking place. The decrease of the titanium ion is evident in these cases because of the increased potential of the titanium electrode in a soultion of

this type that has been made up several days. It was therefore considered essential to make measurements over a short period of time immediately after the solution was prepared.

The data shown in Table III were secured keeping the above considerations in mind:

TABLE III

Salt Used	Solution No.	E. M. F. of cell	Single Potential of titanium	Reading No.
M/4 $TiCl_3$	1	.582	.246	1
M/4 $TiCl_3$	1	.590	.254	2
M/4 $TiCl_3$	2	.560	.224	1
M/4 $TiCl_3$	2	.572	.236	2
M/8 $Ti_2(SO_4)_3$	3	.500	.164	1
M/8 Ti_2SO_4	3	.540	.204	2
M/8 $Ti_2(SO_4)_3$	4	.520	.184	1
M/8 $Ti_2(SO_4)_3$	4	.533	.197	2

The cell in each case shown in the table was of the form,

Ti, — $Ti^{...}$ solution, KCl (sat.), .1N.E.

Readings number 1 and 2 in each individual solution differed in time by about one hour.

After making the measurements indicated above, about two or three drops of ordinary concentrated hydrofluoric acid were added to the titanous solution in each case. The solution turned to a pale green color. The electrode began to gas rather freely in each case so that E.M.F. measurements were not very constant but the deviations from each other were very small. The readings shown in Table IV give the results obtained:

TABLE IV

HF with solution No.	E. M. F.	Single Potential of Ti.	Increase above average potential in original solution
1	.80	.464	.214
2	.84	.506	.276
3	.93	.594	.402
4	.82	.484	.293

The discrepancies in the above readings were probably due to small variations in the amount of HF added in each case. Increasing the amount of HF increases the single potential appreciably. Figures of the order of those shown in Table IV have been obtained in a qualitative way repeatedly, though rarely as high as that shown for solution number three. The preparation of a solution of TiF_3 of any degree of purity was considered out of the question. Most of the investigators of this compound report it as insoluble in water, while those who consider it soluble have used hydrochloric acid in its preparation, in which event it probably was dissolved in hydrochloric acid solution. If the salt were soluble, it is probable that it would completely hydrolyze in solution.

The Effect of Acid Concentration.

An investigation of the quantitative effect of the acid concentration was undertaken in order to show the variations that occurred in the presence of different amounts of acid. A series of solutions were prepared which contained a constant amount of $Ti^{\cdots}$ but varying amounts of acid. A low concentration of the titanous ion was chosen so that the reaction to the acid would probably be more sensitive. Twentieth molar titanous solutions were used. The cell was as usual

Ti, $Ti_2(SO_4)_3$, KCl (sat.), .1 N.E.

Ti, $TiCl_3$, KCl (sat.), .1 N.E.

The results for $Ti_2(SO_4)_3$ with H_2SO_4 are shown in Table V.

TABLE V

Sol. No.	Normality of acid	E. M. F. of cell	Single Potential	Volts change in single potential	Check on E. M. F. 1 hr. later
1	0	.542	.206	——	——
2	.224	.434	.098	.108	.434
3	.261	.430	.096	.110	.432
4	.97	.347	.011	.195	.348
5	1.44	.317	−.019	.225	.316
6	2.36	.278	−.058	.264	.278
7	3.74	.234	−.102	.308	.234

For the M/20 $TiCl_3$ − HCl solutions the single potential change is shown in Table VI.

TABLE VI

Sol. No.	Normality of acid	E. M. F. of cell	Ti Single Potential	Volts change in single Potential	Check on E. M. F. ½ hr. later
1	0	.570	.234		none
2	.425	.460	.124	.110	.461
3	.960	.427	.091	.143	.428
4	1.68	.417	.081	.153	.419
5	2.16	.412	.076	.158	.415
6	2.52	.405	.069	.165	.406
7	5.1	.385	.049	.185	.390

The data in Tables V and VI were checked by using a different portion of each solution as soon as measurements were completed on the series. The check in each instance was within one or two millivolts. Attempting to run a third check twenty-four hours later was made without success in so far as obtaining the same results was concerned, but values of the same relative order seemed to obtain. This was perhaps due to some change in the solutions on the electrode. The results show some tendencies in the effect of the sulfuric acid on the sulphate solution differing from those displayed by the hydrochloric acid on the chloride solution.

The Effect of Dissolved Salts.

Since the depressing action as shown by the above data is contrary to normal action, it was thought that an investigation of the action of the neutral salts of the alkali metals might be of benefit. Accordingly, a series of solutions of varying normality of K_2SO_4 and KCl respectively, were prepared, each of them contained a constant amount of $Ti_2(SO_4)_3$ for the K_2SO_4 trials and $TiCl_3$ for the KCl experiments.

For KCl the results obtained are shown in Table VII.

TABLE VII

Sol. No.	Normality of KCl	E. M. F. of cell	Ti single potential	Volts change in single potential	E. M. F. check later
1	0	.560	.224		.570
2	.32	.595	.259	.035	.606
3	.75	.610	.274	.050	.622
4	1.07	.623	.287	.063	.637
5	1.35	.631	.295	.071	.640

Table VIII shows the results obtained for K_2SO_4 in $Ti_2(SO_4)_3$.

TABLE VIII

Sol. No.	Normality of K_2SO_4	E. M. F. of cell	Ti Single Potential	Volts change in single potential	Check E. M. F. later
1	0	.560	.224		.572
2	.396	.610	.274	.050	.623
3	.645	.625	.289	.085	.637
4	9.25	.636	.300	.076	.651
5	1.32	.642	.306	.082	.655

The addition of KF to the solutions of $Ti_2(SO_4)_3$ and $TiCl_3$ was tried but produced very indefinite results. Small quantities seemed to cause a reduction of the titanium potential but it was very slight. Upon the addition of larger quantities, the E.M.F. increased to the vicinity of that value obtained when HF is added. The change of color of the solution from violet to green accompanies this rise, and gas, probably hydrogen, is evolved from the solution. This is due, no doubt, to the oxidation that takes place so easily in alkaline solutions. It is well known that Ti_2O_3 hydrated is very readily oxidized and liberates hydrogen from alkaline solutions during the process. Addition of sufficient KF converts the hydrogen ion concentration to the alkaline side and thus permits of the oxidation as noted above.

Part III. Replacement Experiments

It is possible to attack qualitatively the problem of relative electrode potentials by immersing a metal in a solution of a salt of another and determine whether or not the second metal is plated out at the expense of the first. Unfortunately, with titanium this method can be approached from but one side,

for other metals do not replace it from solutions of its salts. Titanium will replace other metals in certain solutions, however, and in these cases its electrode potential may be compared to that of the metal replaced.

Table No. IX will show the results obtained.

TABLE IX

The Replacement of Metals from their Salts by Titanium

	Ti in Solution of		Ti in Solution of
$CuSO_4$	No replacement	AgF	Replacement
$AgNO_3$	" "	PbF_2	"
$AgCH_3COO$	" "	CdF_2	"
$HgCl_2$	" "	CoF_2	No replacement
$HgNO_3$	" "	NiF_2	" "
$CdSO_4$	" "	ZnF_2	" "
$AuCl_3$	Very slow replacement	FeF_2	" "
$AuBr_3$	Slow replacement	$PtCl_4$	" "
CuF_2	Replacement	$PtCl_4 + HF$	Replacement

It is noticeable in these experiments that in all solutions, except the fluorides, titanium is extremely inactive. Even in the gold solutions, replacement is very slow and does not, as a rule, show up appreciably for several days. In fluoride solutions, however, the activity is quite pronounced, even cadmium being replaced very rapidly and completely.

It is worth while at this point to compare the action of titanium to that of silicon, as reported by Gilbert, who observed that this element replaces none of the metals from salts other than fluorides. In the presence of hydrofluoric acid, however, it replaces silver, copper, antimony, bismuth and mercury.

The nature of the deposit obtained in each of the positive cases cited above is quite distinct. In the case of gold replacement, the action is very slow. No appearance of any deposit is noticeable for several hours. Gradually a thin deposit will occur which easily drops off the titanium and settles at the bottom of the solution in flakes.

In the case of copper, however, in a copper fluoride solution the deposit on titanium is very adherent and necessitates the use of nitric acid to make a complete removal from the surface. After the surface is well covered replacement apparently stops. Titanium in a silver fluoride solution produces a loosely adhering crystalline deposit which continues until all the titanium is exhausted. It is quite probable that an equivalent quantity of silver is plated out as is the case with silicon.

In the replacement of lead, there appeared none of the usual tendencies of that metal to "tree." Only fine black granules which readily settled out were noticeable.

The replacement of cadmium by titanium was the most spectacular of all. A very small piece of titanium produced from cadmium fluoride a large spongy mass of cadmium which showed the tendency to form into a ball. The deposition was rapid and apparently complete.

Introducing titanium into solutions of the fluorides of cobalt, nickel, iron, and zinc produced nothing except a slight evolution of gas from the titanium. The fluorides were prepared by neutralizing the carbonates of the respective metals—using an excess in each case—with hydrofluoric acid. The evolution of gas was probably due to a trace of free acid. At any rate, the gassing soon stopped and no further action took place.

The attempt to replace platinum from chloride solutions was unsuccessful. Upon the addition of a trace of hydrofluoric acid to the platinum solution into which a piece of titanium had been introduced, an instantaneous deposit of platinum black appeared on the titanium and the solution became colorless.

Mercury fluoride is very unstable. Additon of hydrofluoric acid to its solutions usually causes the appearance of a black precipitate so that it is not possible to observe whether or not replacement is accomplished by titanium in such solutions.

Discussion

According to the potential measurements the single potential of titanium against a M/4 solution of $TiCl_3$ is $.23 + + .03$ volt.considering the normal hydrogen electrode potential as zero. Against a similar solution of the trivalent sulfate the value is somewhat lower, or as an average, .18. This would indicate that titanium should liberate hydrogen from acids, which is in accordance with the facts. Likewise, tin, lead, copper, silver, and mercury should also be readily replaced by titanium in any of their salts. Such is by no means the case. Only in fluoride solutions, where the single electrode potential is much higher, does this peculiar element act with any degree of normal behavior. Here the potential measurements and replacing action are in splendid agreement except in the case of the nickel, cobalt, and iron salts. Silicon exhibits this same property of being more active in fluoride solutions.

Explanation of this difference of action in fluoride solutions may be based upon the same postulate as that adopted by Bird and Diggs.[1] They assumed that all elements act alike so far as replacing mechanism is concerned, regardless of the metallic or non-metallic nature of the element. They explained the replacement of copper in copper sulfate as proceeding according to the equation

$$5\ CuSO_4 + 2P = P_2(SO_4)_5 + 5Cu.$$

The phosphorus sulfate is immediately hydrolyzed to phosphoric acid and sulfuric acid, both readily soluble in water, so the reaction may continue according to the above equation until all of the copper has been removed.

Analogously, if silicon or titanium could be made to replace copper in copper sulfate solution, the reaction would be represented as

$$Si + 2CuSO_4 = Si(SO_4)_2 + 2Cu$$
$$Si(SO_4)_2 + 4H_2O = Si(OH)_4 + 2H_2SO_4$$

and

$$Ti + 2CuSO_4 + Ti(SO_4)_2 + 2Cu$$
$$Ti(SO_4)_2 + H_2O = Ti(OH)_4 + 2H_2SO_4.$$

[1] J. Am. Chem. Soc., **36**, 1382 (1914).

In these two cases the $Si(OH)_4$ or $Ti(OH)_4$ are not easily soluble in water or dilute acid, so the reaction may be completely stopped at its inception by an invisible but protective coating of oxide or hydroxide of the silicon or titanium. This is in harmony with the oxide film theory of the passivity of iron in nitric acid, and similar to this theory, it is difficult to prove or refute.

In the light of this explanation the effect of hydrofluoric acid on these reactions is to dissolve any oxide of titanium or silicon and so prevent the formation of any protective film. If this apparently passive condition of titanium is to be explained by other theories of passivity, such as the formation of a gas film on the surface, it is difficult to understand why this condition should not continue even in the presence of fluorides.

Further evidence in favor of this oxide theory is the fact that titanium reacts with nitric acid in a manner similar to that of aluminum forming even a visible white film, after which there is no further action. It also shows the so-called "valve action" so well known with aluminum in the electrolytic cell. During the course of this investigation, a series of cells was arranged according to the plan

$$Pb,\ Na_2HPO_4,\ Ti - C,\ CuSO_4,\ C,$$

and the extreme terminals attached to a source of alternating current. Copper plated out on one of the carbon electrodes. This proves that a high resistance to the entering current is established at the titanium electrode, due no doubt to the discharge of the phosphate ion at that pole.

Obviously there are certain facts which fail to strengthen this theory, namely, the slow replacement of gold from its chloride solution by titanium, and the fact that replacement of such metals as copper and silver does not occur even in strongly acid solutions, although titanium hydroxide freshly prepared is appreciably soluble in concentrated acids.

It is remarkable that the discrepancies between potential measurements and replacement tendencies exhibited in the fluoride solutions are limited to solutions whose positive ions are composed of metals that show marked passivity, viz. cobalt, nickel, and iron. No record of a measurement of the single potentials of nickel, cobalt, or iron in fluoride solutions is available but it is possible that hydrofluoric acid and its derivatives exert a specific action toward the single potential of those elements that are classed as passive. This specific action is very evident for those elements of the fourth group that are on the dividing line between metals and non-metals—silicon, titanium and zirconium. It is also apparent from the rather exclusive solvent action that hydrofluoric acid exerts on such passive elements as tungsten, tantalum and niobium. All of these metals are readily attacked by hydrofluoric acid and either not at all or very slowly by other acids.

Explanation of the effect of acid in decreasing the electrode potential of titanium is a very difficult undertaking since it would be expected from ordinary theoretical considerations that the electrode potential would be increased. Richards and Dunham[1] in their study of the effect of acid concentration on the single electrode potential of zinc in zinc sulfate conclude that

a large part of the increase in that case is due to liquid potentials. The same condition existed in this case undoubtedly for substitution of a saturated potassium sulfate solution for saturated potassium chloride as the intermediary bridge electrolyte prodcued appreciable effects in the E.M.F. of the cell, but these effects are small in comparison to the effects caused by the addition of acids to the titanium solutions. However, in similar measurements, of the single electrode potential of gallium, Richards and Boyer found that increased acid concentration had an effect similar to that found in the case of titanium. For this fact no explanation was offered.

It is probable that most of the change is due to transformations that take place in the solutions. Data and experimental observations do not warrant more than a guess as to the real thing that is at the bottom of this unusual action. However, it is known that titanium salts form complex double salts and acid salts which may act in numerous unknown ways. For example, one salt, $3\ Ti_2(SO_4)_3\ H_2SO_4\ .25H_2O$, has been mentioned earlier in this paper. Just how the complexes might increase the concentration of the titanium ion, in absence of specific information regarding the complex, can not of course be postulated.

Two different forms of $TiCl_3$ have been mentioned in the literature. One of these is the well known violet compound, the other a brown-colored solid. The isolation and study of the latter have not been completely successful owing to its elusive or unstable nature. It seems plausible that the two forms may possibly exist in equilibrium in solution, and this equilibrium may be considerably disturbed by addition of acid. That there is some change in the constitution of the dissolved substance is proved by the fact that acid concentration affects the color of the solution to a very considerable extent. $TiCl_3\ .6H_2O$ when dissolved in pure water produces a dark blue solution. Addition of acid to this solution in successive quantities produces a pink-violet color which gradually changes to an intense blue violet at high concentrations of acid. Just what takes place in the solution is unknown, but it is possible that some equilibrium between two forms of titanium trichloride may exist and that this equilibrium may be affected greatly by hydrochloric acid. One of these forms may ionize in a manner entirely different from that of the other. Such a case is known in chromium chloride, although nothing is known concerning the effect the two forms may have on single potentials.

An attempt to find a break in the single potential-hydrogen ion results that would reveal any definite or sharp transformation was without success. This would hardly be expected to occur in an equilibrated system; however examination of the results showing the effect of acid concentration on the single potential will show a difference in the tendency of the $Ti_2(SO_4)_3 - H_2SO_4$ system from that of the $TiCl_3 - HCl$ system. The values show above all that the hydrogen ion is not being measured, because the decrease in E.M.F. produced by acid is greater in the case of sulfuric than it is with hydrochloric which is more highly ionized.

The neutral alkali salts show the opposite effect from that of the acid when added to the titanous salts, or in other words, they act as one would expect

when a common ion is added to an electrolyte. However, the increase produced in the single potential by the salts is quite small in comparison to the decrease produced by acids. This indicates that the action of alkali salts containing a common ion is only a matter of common ion effect. The magnitude of their effect is of the order that is exerted on the single potential of other metals, such as zinc, as shown by Richards and Dunham.

The question has been raised as to the validity of using the trivalent ion in single potential since it is held by some investigators that titanium enters solution as the divalent ion. The literature is at a variance on this point, but it seems to be well established that $TiCl_3$ and $Ti_2(SO_4)_3$ is the end product when the corresponding acids dissolve metallic titanium. Even the fluoride produces the trivalent form in the presence of sulfuric acid, although according to the literature its individual action on titanium is to produce TiF_4. In view of these facts it was considered best to use trivalent titanium, especially since this element does not reduce its own salts below that valence.

Summary

1. Metallic titanium has been prepared according to the method of Nilson and Pettersson and optimum conditions governing its preparation in a crystalline form have been studied and fixed. Various modifications of this method were tried and the results are presented. Some very pure crystalline titanium was obtained by this method in pieces varying in size up to five grams.

2. Single potential measurements of titanium were made in M/4 solutions of titanium tri-chloride and M/4 trivalent sulfate. Considering the normal hydrogen electrode potential as zero and the more active elements as positive titanium has an average potential in the trichloride solution of .23 and of .18 in the sulfate.

3. The single potential of titanium is increased approximately .22 volts when a small amount of hydrofluoric acid is present in the titanous solution.

4. Hydrochloric and sulfuric acids added to their respective salt solutions cause a decided decrease in the single potential of titanium.

5. Alkali salts of common ion with the titanium salt cause a slight increase in the titanium potential.

6. Replacement experiments do not agree with single potential measurements in any solution except the fluorides in which case agreement obtains with three exceptions and these replacement reactions show a marked similarity to analogous reactions of elemental silicon.

VISCOSITIES, ELECTRICAL CONDUCTIVITIES, AND SPECIFIC VOLUMES OF ACETIC ACID-STANNIC CHLORIDE SOLUTIONS

BY J. D. STRANATHAN AND JOHN STRONG

The dependence of viscosities of solutions upon the concentration of the solution components is most logically considered under four heads:— (1) Those for which the viscosity of the solution is the same as that calculated from a weighted mean of the viscosities of the components, that is, from the additive law; (2) Those for which the viscosity at any concentration is greater than that calculated from the additive law; (3) Those for which the viscosity at any concentration is less than that calculated from the additive law; (4) Those for which the viscosity at some concentrations is greater and at other concentrations less than that given by the additive law. For solutions of the first type there is no change in volume upon mixing; that is, the specific volume of the mixture is a weighted mean of the specific volumes of the two components. Also, the mixing is accompanied by neither evolution nor absorption of heat. For solutions of the second type there is a contraction upon mixing and an evolution of heat. For mixtures of the third type there is an expansion upon mixing and an absorption of heat. The expansion or contraction is usually interpreted as a decrease or an increase in association.[1]

The acetic acid-stannic chloride solutions studied by the authors are examples of type two solutions. Their viscosities are often hundreds of times larger than those calculated from the additive law, there is marked evolution of heat upon mixing, and the volume contraction for some concentrations is as much as 32.10% of the volume calculated from the additive law. In fact solutions of acetic acid and stannic chloride are quite abnormal in that their physical properties deviate from the weighted mean by a far greater percentage than is the case for any other similar solution known to the authors.

Preparation of Solutions:—Anhydrous Stannic Chloride and 99.7% Glacial Acetic Acid were used to make the solutions. Some indication of purity is given by the fact that the specific electrical conductivity of the acetic acid was of the order of 4×10^{-8}, while that of the stannic chloride was of the order of 2×10^{-9} reciprocal ohms. Twelve mixtures varying in mol fraction concentration of $SnCl_4$ from 0.0244 to 0.4111 were prepared in wide mouth, glass stoppered bottles. At concentrations slightly higher than 0.4111 the mixture breaks into two liquid layers, the lower one of which is nearly pure $SnCl_4$.

Great care was necessary in making up the solutions to avoid unnecessary impurities. $SnCl_4$ and solutions rather rich in it fume vigorously when exposed to moist air. Likewise, acetic acid takes up water rather readily. To avoid these difficulties, the weighted bottle into which the solution was to be put was filled with dry air. The stannic chloride was siphoned in through a glass

[1] Bingham: "Fluidity and Plasticity," 160 (1922).

tube extending into the bottle through a tight-fitting stopper. Only dry air was let into the container from which the stannic chloride was siphoned. After weighing the bottle and stannic chloride, acetic acid was let in in the same manner. In this way all fuming was avoided.

Viscosity Measurements:—The design of apparatus for viscosity measurements of acetic acid-stannic chloride solutions must take into account the following items:—(1) The viscosities to be measured vary widely, depending upon concentration; at a temperature of 25.2°C. they vary by a factor over 300. The apparatus must be adaptable to such widely varying viscosities. (2) $SnCl_4$ solutions fume vigorously when exposed to moist air. In addition to changing the composition of the solution, this fuming results in the formation of stannic oxide which would clog the capillary of the viscometer. The measurements must therefore be carried out with minimum exposure to moist air. (3) Solutions of certain concentrations are exceedingly viscous. Very slow draining would therefore introduce considerable error in the apparent volume flowing through the capillary if the solution were allowed to drain from a vessel of known volume. The volume flowing through the capillary would be known more accurately if the solution were allowed to flow into, rather than out of, a vessel of known volume.

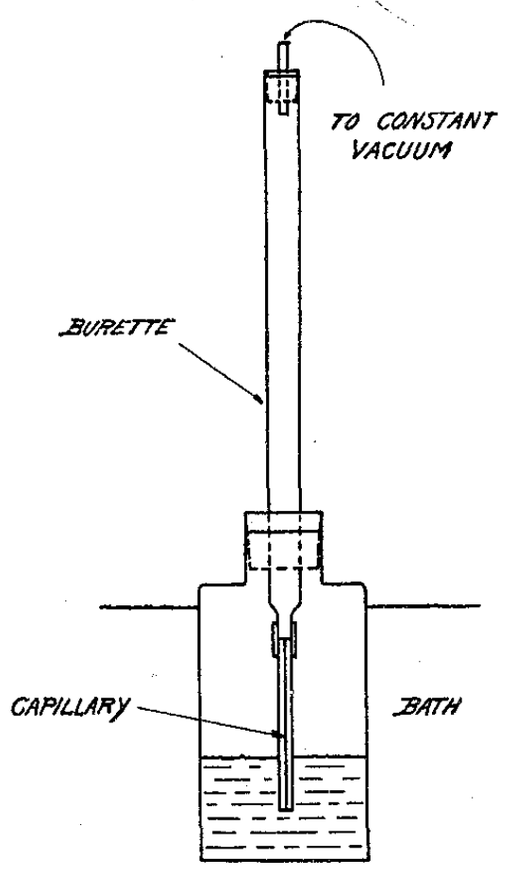


FIG. 1

The apparatus which seemed best adapted to the needs is indicated in Fig. 1. The bottle containing the solution was nearly submerged in a water bath held at a constant temperature of 25.2 ± 0.05 C° by a thermostat. The solution was forced upward through the capillary into a graduated burette by creating a constant, partial vacuum in the burette. The difference between the pressures on the surfaces of the liquid in the bottle and in the burette was read directly from a water manometer. The apparatus was adapted to the measurement of widely different viscosities in that capillaries of different diameters could be used; also, the difference of pressure forcing the liquid through the capillary could be varied. Five different capillaries were used, their diameters varying from 0.284 mm. to 2.474 mm. The largest of these was used only for measurements at zero degrees. Each capillary was slightly under 8 cm. long and was cut off square at the ends.

Data were taken as follows. A difference of pressure was applied by creating a constant, partial vacuum in the graduated burette. The times were recorded from a stop-watch whenever the liquids rising in the burette passed a

graduation indicating a cubic centimeter. From these data the times required for each cc. to flow through the capillary were obtained. These time intervals increased as more and more liquid flowed into the burette, due to the back pressure exerted by the rising column. The resiprocal of the rate of flow ($\triangle t/\triangle v$) was then plotted against the number of cc. which had flowed into the burette since starting to count time, each value of $\triangle t/\triangle v$ being plotted in the middle of the volume interval to which it corresponds. An example of the resulting curve is shown in Fig. 2. As the liquid flowed back through the capillary in to the containing bottle, heights of the liquid in the bottle and in the burrette were recorded at various intervals along the burette

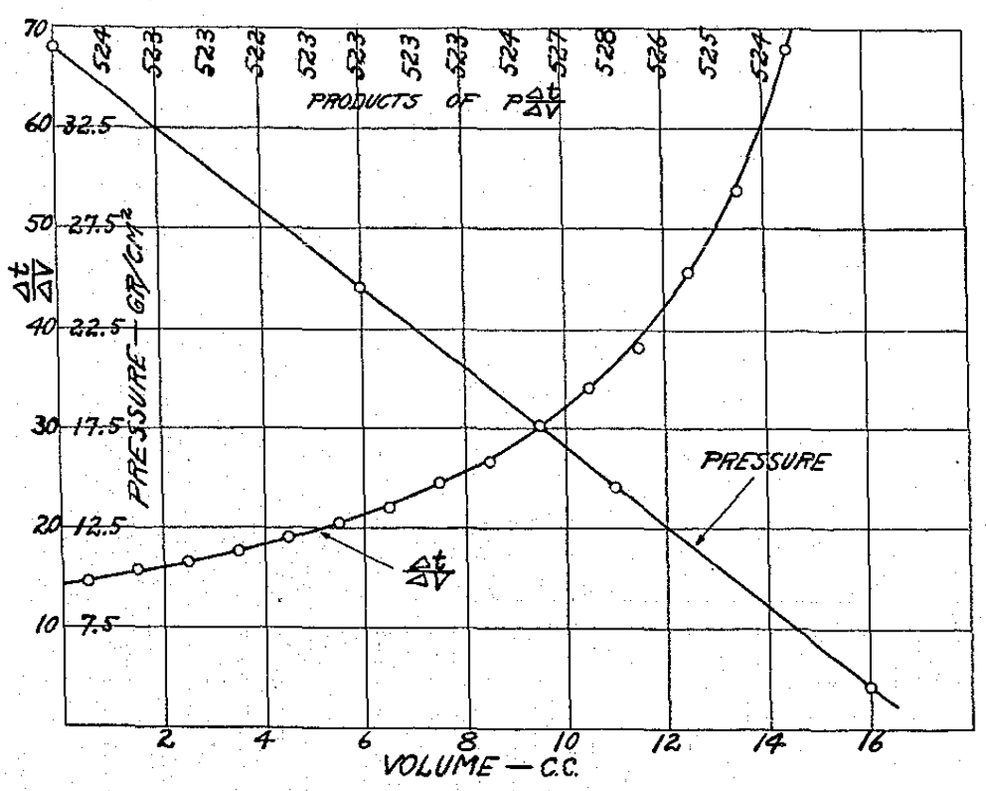


FIG. 2

scale. From the difference of height, the density of the liquid and the pressure occasioned by the partial vacuum in the burette, the actual pressure forcing the liquid through the capillary was calculated at various intervals along the burette. These pressures were likewise plotted against the volume of liquid in the burette. The curve is shown in Fig. 2.

The Poiseuille equation relating the absolute viscosity η of a liquid of density d to the rate at which it flows through a capillary of radius r and length l under the influence of a pressure p grams per sq. cm., is

$$\eta = \frac{\pi g r^4}{8(l+\lambda)}\left(p\,\frac{\Delta t}{\Delta v}\right) - \frac{d}{8\pi(l+\lambda)}\left(\frac{\Delta t}{\Delta v}\right)$$

where λ is the Couette correction for the effective length of the capillary and where the second term is the correction due to the kinetic energy of the liquid streaming through the capillary. If the kinetic energy correction be small it

is apparent that the product $p\frac{\Delta t}{\Delta v}$ is proportional to viscosity, and therefore constant irrespective of what pressure is used to force the liquid through the capillary. That is, the products of the ordinates of the two curves shown in Fig. 2 should be constant. The products calculated at regular intervals from the experimental curves shown are tabulated across the top of Fig. 2. Their constancy is an indication of the accuracy of the work. The average variation from the mean in this case is 0.27%. The average value of $p\frac{\Delta t}{\Delta v}$ obtained from experimental curves was used in the calculation of viscosity.

The correction λ to add to the measured length of the capillary is given[1] by 1.64 times the radius of the capillary, in case the ends are cut off square. Correction was made for this, though it amounted to only 1.3% for the largest capillary, and much less for all others. Likewise, correction was applied for the kinetic energy of the liquid issuing from the capillary. Rarely did this correction exceed a few tenths of 1%, though for one or two of the weaker solutions (weaker in $SnCl_4$) it did amount to a little over 1%. The corrected absolute viscosities found for solutions of stannic chloride in acetic acid are shown in the second column of Table I. The data is for a temperature of 25.2 ± 0.05 C°.

By way of checking the reliability of our method, a determination of the viscosity of water at 25.2° C. was made. The average of two determina-

TABLE I

Mol Fraction Concentration of $Sn Cl_4$	Absolute Viscosity	Specific Volume	Specific Electrical Conductivity
.0000	0.01155	0.9486	———
.0244	.02121	.8841	11.85×10^{-4}
.0520	.04373	.8096	25.29
.1084	.1897	.7107	20.74
.1719	.963	.6330	8.68
.2290	2.582	.5830	3.670**
.2527	3.034	.5655	2.887
.2682	2.909	.5580	2.510
.2969	2.105	.5446	2.591
.3151	1.649	.5361	2.858
.3498	.864	.5250	3.678
.3608	.691	.5206	3.967
.4111	.4234	.5152	4.550
1.0000	.0084*	.4436	———

[1] "Dictionary of Applied Physics," 1, 1047.

*Rather poor result, due to tendency for capillary to clog.

**There is reason to believe that this value is low.

tions was 0.00886. This compares very favorably with the value 0.00889 interpolated from values given for different temperatures in the Smithsonian Tables. Likewise, our value of 0.01155 for pure acetic acid compares somewhat less favorably with the value 0.01121 interpolated from data given in the Smithsonian Tables, or with the value 0. 01194 given by Gross.[1]

The curve of Fig. 3 shows the observed manner of variation of viscosity with concentration. Since the viscosities of both components are negligibly small as compared to the viscosity of the solution at all except very small con-

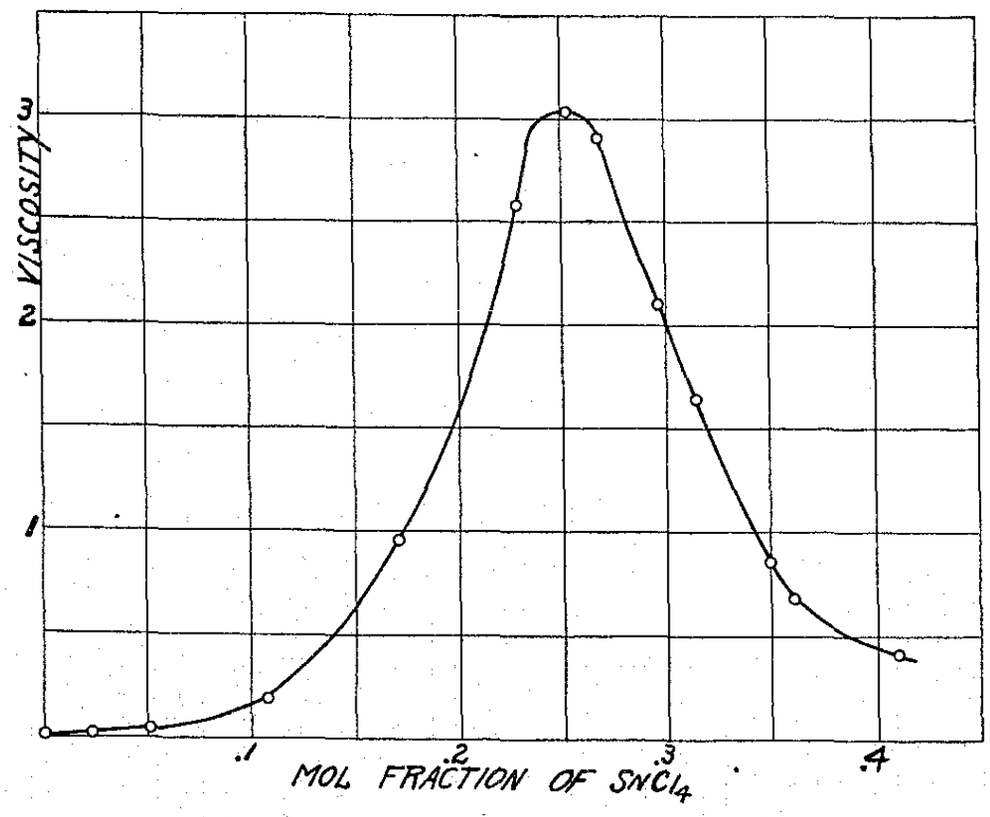


FIG. 3

centrations, it follows that this curve also represents practically the deviation of the viscosity from the value calculated from the weighted mean of the viscosities of the two components. The magnitude of the deviation from the value calculated from the additive law is unusually large. The peak value of the curve is larger than the value calculated by the additive law by a factor of 282. The viscosity represented by the peak is greater than that of the most viscous component by a factor of 263, using our value for the viscosity of acetic acid. This factor of increase is much greater than that for any other non-colloidal solution known to the authors. The most marked of any systems found in the literature for a temperature around 25°C are those of aniline-acetic acid and o-chlorophenol—quinoline. Certain concentrations of aniline-acetic acid solutions[2] have viscosities 6.1 times that of the most viscous component; certain concentrations of o-chloro-

[1] Paul M. Gross: Dissertation, Columbia University (1919).

[2] Thole, Mussell, and Dunstan: J. Chem. Soc., 103, 1114 (1913).

phenol—quinoline solutions[1] show approximately the same ratio. At 0°C certain o-chlorophenol—quinoline solutions have viscosities 28 times that of the most viscous component. Viscosity diagrams for which one of the components is $SnCl_4$ have been obtained by N. S. Kurnakov, S. I. Perlmetter, and F. P. Kanov,[2] and by N. S. Kurnakov and N. N. Beketov.[3] These diagrams show maxima. The curves were available to the authors, however, and therefore no information regarding the magnitude of the maxima is at hand.

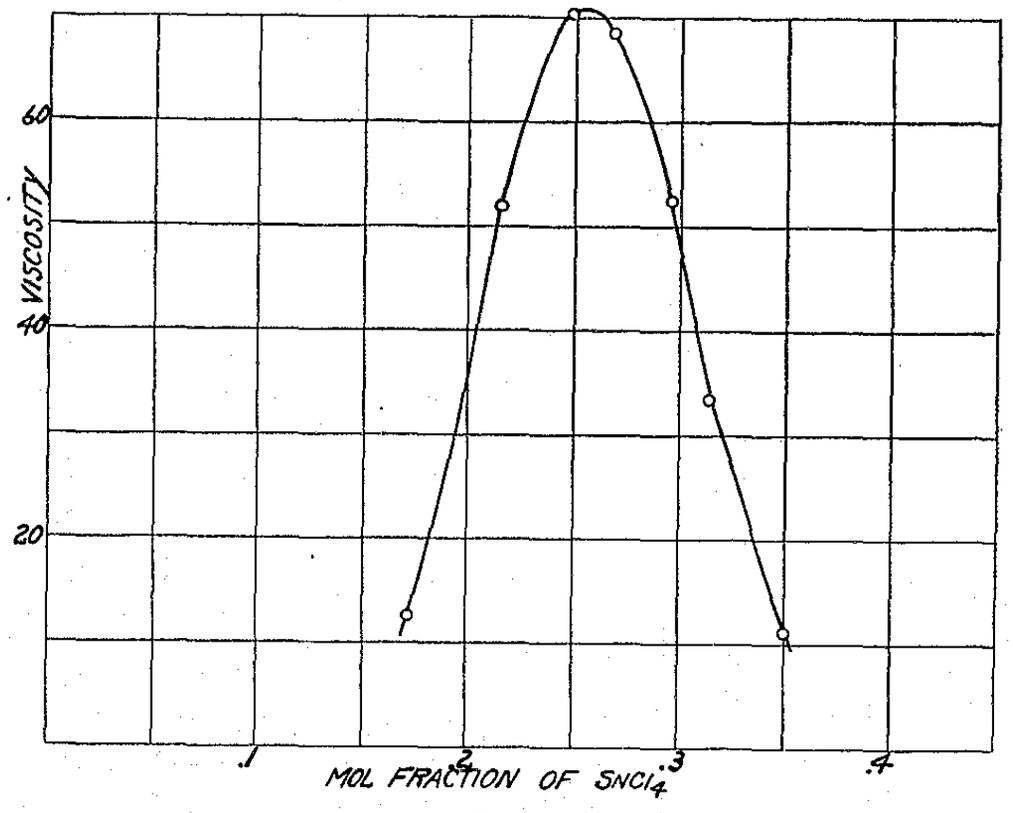


FIG. 4

The position of the maximum viscosity, which is here indistinguishable from the position of the maximum deviation from the weighted mean of the component viscosities, is accurately at a concentration 0.25. This concentration is precisely that which would be given by a compound $SnCl_4.3CH_3COOH$. In view of the extremely large deviation from the additive law, the accuracy with which the peak falls at the concentration corresponding to this compound, and the unusually great volume contraction and heat evolution upon mixing, it seems logical to attribute the marked change in properties with concentration to the formation of a compound $SnCl_4.3\ CH_3COOH$.

An attempt to determine the fusion curve was made to see whether it gave any indication of a compound. Supercooling and the fact that the viscosities increased gradually until the samples became amorphous solids precluded the possibility of such determinations.

[1] A Bramley: J. Chem. Sac. 109, 451 (1916).
[2] J. Russ. Phys. Chem. Soc., 48, 1658 (1916).
[3] J. Russ. Phys. Chem. Soc., 48, 1694 (1916).

In order to see whether the position of the maximum of the viscosity curve, and thence the position of the maximum deviation from the weighted mean of the component viscosities, shifts with temperature, some measurements of less precise nature were carried out at 0° C. The bottle containing the solution was placed in a mixture of ice and water. After allowing considerable time for the temperature to fall to 0° C., the viscosity was measured. The results are plotted in Fig. 4. It is apparent that the maximum viscosity increased by a factor of about 23 for a drop in temperature of approximately 25°. This corresponds to an extremely large temperature coefficient. The position of the maximum of this curve is rather doubtful. Remembering that it is characteristic of most viscosity curves to be unsymmetrical about the maximum[1] (and the solutions here studied show some dissymmetry at 25.2°), it seems probable that the maximum of this curve is very close to a concentration of 0.25. If the position of the actual maximum is shifted toward higher concentration at 0°, the shift is certainly very small; it is considerably less than 0.01 in concentration even though the viscosity is increased by a factor of 23. In view of the tremendous temperature coefficient of viscosity and the difficulty in getting the very viscous solutions to cool uniformly to 0°, it appears probable to the authors that there is no actual shift in the position of the maximum with temperature changes.

Contraction of Solutions upon Mixing:—The densities of the solutions were measured at 25.2° C. with a sensitive Joly Balance. From the absolute specific volumes (Table I), the per cent contraction of solutions upon mixing were calculated and tabulated in Table II. The maximum percentage contraction of 32.10 is unusually large. The position of this maximum is approximately at a mol fraction concentration of 0.31. The fact that this maximum does not occur at identically the same concentration as does the maximum viscosity deviation is contrary to the view presented by Denison[2] that the maximum deviations in the various property curves should occur at the same concentration. Many other solutions show this same disagreement, however; among them are Aniline-Acetic Acid and o-Chlorophenol—Aniline.[3]

TABLE II

Mol Fraction Concentration	Percent Contraction	Mol Fraction Concentration	Percent Contraction
.0000	.00	.2682	31.38
.0244	5.57	.2969	31.81
.0520	12.22	.3151	32.10
.1084	20.50	.3498	31.99
.1719	26.55	.3608	32.07*
.2290	30.01	.4111	30.48
.2527	31.12		

*When the observed specific volumes are plotted against concentration, it is apparent that the value for this concentration is slightly low. Using the specific volume taken from the smooth curve, the percent contraction is 31.82 instead of 32.07.

[1] See, for example, data for Analine-Acetic Acid System, Thole, Mussell, and Dunstan: J. Chem. Soc., **103**, 1113 (1913).
[2] R. B. Denison: Trans. Faraday Soc., **8**, 20 (1912).
[3] Thole, Mussell, and Dunstan: J. Chem. Soc., **103**, 1114 (1913).

Electrical Conductivity of Solutions:—Electrical specific conductivities of the solutions were measured by the usual Kohlrausch bridge method. The conductivity cell was standardized with a 1/50 normal solution of KCl. The experimental specific conductivities are shown in the fourth column of Table I. They are plotted against mol fraction concentration in Fig. 5. The specific conductivity is a function of the ion concentration, the ion mobility, and the viscosity. The first of these factors probably accounts for the initial rapid increase in conductivity, while the rapid increase in viscosity undoubtedly accounts for the subsequent decrease in conductivity.

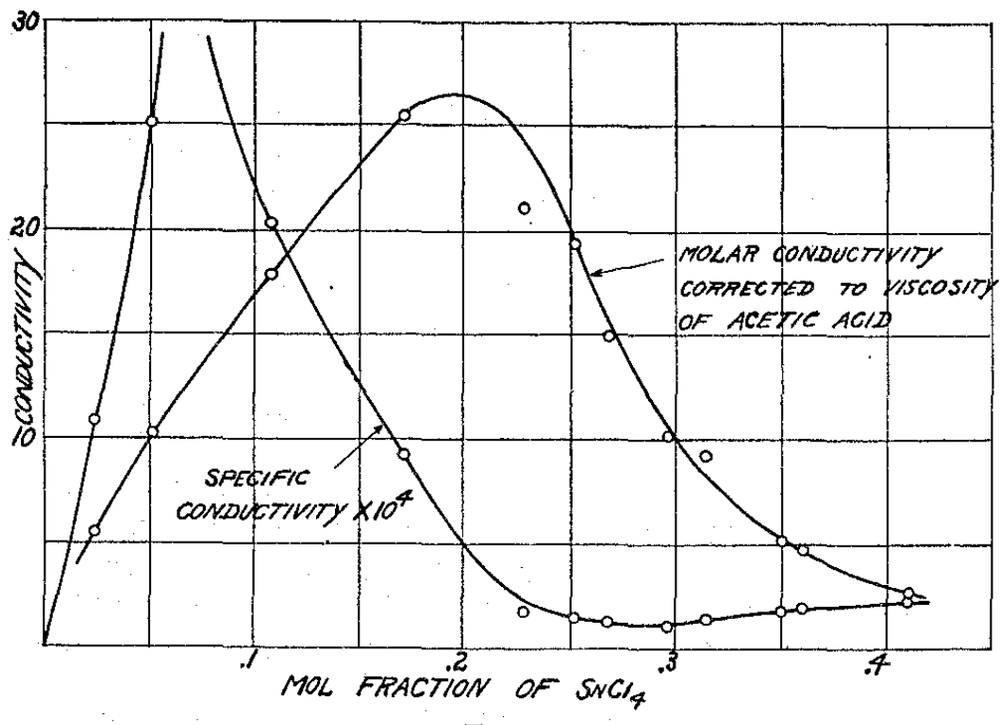


FIG. 5

Other things being equal, it is known that the ion mobility is inversely proportional to the pth power of the viscosity, where p is a constant dependent upon the nature of the ion. In those cases for which p is known its value is not far from unity.[1] If we assume the exponent to be unity, the conductivity can be corrected to the viscosity of the pure solvent (acetic acid). The second curve of Fig. 5 shows the molar conductivity so corrected. For most substances the molar conductivity corrected to the viscosity of the pure solvent continually decreases with increasing concentration. The fact that the molar conductivity here increases indicates either that the dissociation is increasing or that the nature of the ion is changing. The formation of more mobile ions is hardly consistent with the interpretation given the marked viscosity increase and volume contraction, namely, an increase in association. It therefore seems probable that the increase in molar conductivity indicates an in-

[1] Kraus: "The Properties of Electrically Conducting Systems," 114 (1922).

crease in dissociation. This is in agreement with the hypothesis advanced by Kendall[1] that dissociation in solution is preceded by association, in that the two phenomena do accompany one another here.

Summary:—The viscosities, electrical conductivities, and specific volumes of solutions of stannic chloride in acetic acid have been measured for various concentrations of $SnCl_4$ up to that for which the mixture breaks into two layers.

The mixing is accompanied by large volume contraction and heat evolution. The volume contraction at certain concentrations amounts to 32.10% of the volume calculated from a weighted mean of the component specific volumes.

The curve relating viscosity to concentration has a very marked maximum. The maximum deviation of the measured viscosity from that calculated from a weighted mean of the component viscosities is remarkable large. The maximum is 282 times as great as that calculated from the additive law; it is 263 times the viscosity of the most viscous component.

The maximum of the viscosity curve, and therefore the maximum deviation of viscosity from that calculated from a weighted mean of the component viscosities (since the component viscosities are negligible as compared to the solution viscosity), occurs accurately at a concentration of 0.25. The position of the maximum is probably independent of temperature.

In view of the extremely large deviation of viscosity from the additive law, the accuracy with which the peak falls at the concentration corresponding to the compound $SnCl_4.3CH_3COOH$, and the unusually great volume contraction and heat evolution upon mixing, it seems logical to attribute the marked change in properties with concentration to the formation of a compound $SnCl_4.3CH_3COOH$.

University of Kansas.
May 28, 1927.

[1] Kendall, Booge, and Andrews: J. Am. Chem. Soc., 39, 2302 (1917); Kendall and Booge: 39, 2326 (1917).

GERMANIUM. XX.[1] PREPARATION OF FUSED GERMANIUM DIRECTLY GERMANIUM DIOXIDE[2]

BY KATHARINA M. TRESSLER AND L. M. DENNIS

Up to the present time, fused, massive germanium has been prepared by first reducing germanium dioxide by heating it in hydrogen and then fusing the residual powder under sodium chloride[3] at a temperature of about 1000°. This reduction in hydrogen is a tedious and time-consuming process, and various attempts have been made in the Cornell Laboratory to shorten the procedure.

Reduction with granular aluminum goes smoothly to completion, but there is heavy loss of germanium because of volatilization of the intermediate reduction product, germanous oxide.

The same difficulty was encountered in experiments upon the electrolytic preparation of metallic germanium. Germanium dioxide dissolves readily in molten potassium fluogermanate, or in molten cryolite, and the metal separates in small pellets upon electrolysis in a graphite cell with a graphite cathode. The yield, however, was low because of loss of germanous oxide.

Since germanium apparently does not unite with carbon to form a carbide,[4] it was thought that it might be possible to reduce the dioxide with carbon under a layer of dry sodium chloride at a temperature high enough to yield the metal in fused, massive form, and at the same time develop a technique which would permit of the recovery of any germanous oxide which might be volatilized during the reaction.

Germanium dioxide and sugar carbon were intimately ground together and were then mixed with approximately an equal weight of pure sodium chloride. These charges were placed in special unglazed porcelain crucibles 7 cm. high and 3 cm. in diameter and were tamped down, the charge in each case filling the crucible about half full. The crucible was then filled to the top with sodium chloride which was also tamped. In the early experiments the crucible was heated by a gas-air blast lamp and was held at a temperature of approximately 1000° for 30 minutes. The crucible was at first covered (Expt. 1) but as there was some volatilization of germanous oxide, a large tube of hard glass was slipped over the top of the crucible, and air was drawn upward through this tube. Any germanous oxide which volatilized condensed in the tube either as such or as germanium dioxide formed through oxidation. The results of three runs by this method were as follows:

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[1] Contribution from the Department of Chemistry, Cornell University.

[2] This article is based upon part of the thesis presented to the Faculty of the Graduate School of Cornell University by Katharina M. Tressler in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Dennis, Tressler and Hance, J. Am. Chem. Soc., **44**, 2033 (1923).

[4] Dennis, Tressler and Hance: loc. cit.

Expt. No. 1

Charge		Yield
7.2 g. GeO_2 (containing 2.44% of H_2O)	4.32 g. metal	88.6%
1.75 g. sugar carbon	GeO_2 recovered from salt	6.1%
10 g. salt	Total	94.7%

Expt. No. 2

Charge		Yield
Same as No. 1	4.342 g. metal	88.97%
	GeO_2 recovered from salt .3303 g.	4.79%
	GeO_2 from tube .1732 g.	2.51%
	Total	96.27%

Expt. No. 3

Charge		Yield
7.2 g. GeO_2	4.300 g. metal	85.61%
10.6 g. tartaric acid	GeO_2 recovered from salt .6190	9.02%
10 g. salt	GeO_2 from tube .0066	0.1 %
	Total	94.73%

To obtain more even heating and more definite control of temperature, a graphite crucible 14 cm. high and 5 cm. inner diameter was used, the crucible being covered with a flanged lid that had an opening in the middle over which a tall, hard-glass tube was placed. Air was drawn up through this tube as in the earlier experiments. The crucible was imbedded in sand and was heated in an induction furnace. Since it was impossible to make measurements of the temperature of the inside of the crucible during the run, an empty crucible was heated in the furnace and the inner temperatures were read with an optical pyrometer. With a current of 4.5 kilowatts per hour, the temperature at the bottom of the crucible remained constant at about 1130°, while half way up the side of the crucible the temperature was about 1000°. In the first run 4.5 kilowatts per hour were used.

Expt. No. 4

Charge	Conditions	
21.69 g. GeO_2 (3% H_2O)	40 minutes heating	
25 g. NaCl	$4\frac{1}{2}$ kilowatts per hr.	
Yield		
Metal (Consisted of small granules scattered through the flux.)	12.7605 g.	85.0%
Wt. GeO_2 recovered from tube	.3238	1.5%
Wt. GeO_2 recovered from NaCl	2.450	11.63%
Total Germanium accounted for		98.13%

The metal in this experiment was not completely fused together. The current was therefore stepped up to 6 kilowatts per hour and the heating was somewhat longer.

Expt. No. 5

Charge	Conditions
Same as Expt. 4	55 minutes heating 6 kilowatts per hour
Yield	
Wt. of metal ingot obtained 13.50 g.	90.0 %
Wt. GeO_2 recovered from tube .3967 g.	1.83%
Wt. GeO_2 recovered from NaCl 1.2490 g.	5.80%
Total Germanium accounted for	97.63%

Expt. No. 6

Charge		Conditions
Same as Expt. 4		4.5–5.5 kilowatts per hour for 30 minutes. 6 kilowatts per hour for for 25 minutes longer.
Yield		
Wt. of metal obtained	13.46 g.	88.40%

In experiment No. 6 part of the charge did not fuse and drop toward the bottom of the crucible.

Expt. No. 7

Charge		Conditions
Same as Expt. 4		4.5–5.5 kilowatts per hour for 30 minutes. 6 kilowatts per hour for 25 minutes longer
Yield		
Wt. Metal	13.45 g.	89.70%
Wt. GeO_2 recovered from tube	.4970 g.	2.3%
Wt. GeO_2 recovered form NaCl	1.1655 g.	5.85%
Total Germanium accounted for		97.85%

An arc spectrogram of the metal, kindly made for us by Professor Papish, showed that the germanium was free from other substances in amounts greater than 0.01%, apart from any germanium oxide that might be present. Solution of a sample of the product in hydrogen peroxide indicated that the metal contained approximately one per cent. of germanium dioxide.

The results show that about two per cent. of the germanium is volatilized, and that about six per cent. is recoverable for the flux. The germanium unaccounted for, two to three per cent., probably escaped extraction after the

fusion, for, with the small charges which were used, it was present in only small amount in a large quantity of the flux. It is also possible that some germanous oxide volatilizes through the walls of the graphite crucible. This difficulty could be avoided by fitting a porcelain crucible inside the graphite crucible.

The chief advantage of this method of preparing metallic germanium from germanium dioxide lies in the fact that any desired amount of dioxide, limited only by the size of the crucible, may be reduced in a short time and the metal obtained in massive form.

Summary

A new method for the preparation of fused metallic germanium directly from germanium dioxide by reduction with carbon under a flux of sodium chloride is described. The yield of metal by this method is about 90% and about 7% of germanium charged is recoverable. With larger charges and slight modification in the procedure, the loss of germanium will probably be negligible.

Ithaca, New York.

ON THE NATURE OF ACTIVATED MOLECULES

L. J. WALDBAUER AND I. J. PATTON

The radiation hypothesis of chemical reaction, as held by Trautz, Perrin, Lewis, and others, is that the increase in internal energy which a molecule must receive before it is capable of reacting (i.e., the critical increment E) is communicated to it by infra-red radiation present in the system, the addition of energy being made in terms of quanta.

In accordance with this hypothesis, chemical action depends upon the absorption of a nearly monochromatic radiation of frequency ν, given by the relation $E_c = Nh\nu$, where E_c denotes the critical increment per gram-molecule. There should, therefore, be found a line of this frequency, or a band including it, in the absorption spectrum. Now, while this sometimes occurs, there is a very large number of cases in which there is no such correlation whatever.[1]

Furthermore, since an increase in the velocity of the reaction with temperature must, on this hypothesis, be due to increased radiation density $U_\nu d\nu$, the temperature coefficient of the velocity constant should be the same as that of the radiation density.

Trautz and Lewis[2] have calculated the rate of bimolecular reactions from the frequency of collision between active molecules and obtained a relation agreeing with experiment. But this agreement in no way proves their hypothesis, for, in plain language, their result means that the velocity of reaction depends on the number of collisions between molecules which, by whatever mechanism, are already capable of reacting; a statement that is almost axiomatic. They do assume "heats of activation," Q_a and Q_b per gram-molecule of substances A and B respectively; but since in their equations only the sum of these two appears, it will be seen that we have again simply our old friend, "heat of reaction," which may be considered quite apart from any imagined mechanism.

This lack of any necessity to assume a radiation mechanism in the case of bimolecular reactions, has been pointed out by Dushman[3] who, however, considers some such assumption necessary in the case of monomolecular reactions. Since, however, outside of radioactive disintegrations, the very existence of monomolecular reactions is extremely problematical, it is doubtful whether a radiation hypothesis is applicable even there. True monomolecular reactions are to be expected between gases, if anywhere; yet every case investigated had been found to be a catalyzed reaction, induced either by the walls of the vessel, by impurities in the reactants, or by the reaction products themselves. Furthermore, the fact that the only reactions yet

[1] Langmuir: J. Am. Chem. Soc., **42**, 2090 (1920).
[2] J. Am. Chem. Soc., **43**, 397 (1921).
[3] Taylor: "Treatise on Physical Chemistry," **2**, 1036 (1924).

recognized as truly monomolecular (namely, disintegration of radioactive elements) are known to continue unaltered, in the dark, and at temperatures approaching the absolute zero, seems to indicate very clearly that the absorption of energy quanta plays no part, and that the explanation must be sought in the interaction of electrons and protons in the crowded and complex nucleus.

It appears to the authors that a very simple explanation of the existence of active molecules can be obtained without recourse to any hypothesis of radiation. In the Bohr atom, the electrons move in elliptical orbits, with the nucleus at one focus. Their velocity is greatest near the nucleus and least in the outer portion of the ellipse. The valence electrons are, of course, furthest from the nucleus, and therefore less firmly held, on the average, throughout their journey; but at the outer limits of their orbits, they are at their greatest distance from the nucleus, and at their slowest speed. Collisions between molecules in this state will be almost certain to cause reaction, and such molecules can be called "activated."

This does not exclude the absorption of radiation quanta as an auxiliary influence. Its effect will be merely to move the valence electron into an outer orbit, further removed from the attraction of the nucleus, and consequently to produce a somewhat higher degree of activation.

The increase of velocity caused by rise of temperature will be due only in small measure, if at all, to the absorption of low frequency radiation, but will depend almost entirely on the rapid increase in the number of collisions and in the force of each collision, due to the increased velocity of the molecules. A very simple calculation on the basis of the gas laws will show, for instance, that in the case of hydrogen, when the temperature is raised 10°, from 40° to 50°C., the kinetic energy is increased by 63.5 m (m = mass of H_2 molecule), and the momentum is increased by 0.97 m. It will be seen that factor is sufficient in itself to account for the approximate doubling of the reaction rate on a 10° rise in temperature.

Unfortunately, like the radiation hypothesis, this explanation of the activated molecule is not at present susceptible to experimental or mathematical demonstration, since the question of the probability of an electron or electrons being in that section of their orbits where they are most likely to react involves the yet unsolved problem of the motion of "n" bodies.

43 rue du Capitaine Ferber,
Paris (XXe), France.

NEW BOOKS

An Introduction to the Study of Experimental Medicine. *By Claude Bernard. Translated by Henry Copley Greene. 27 × 17 cm; pp. xix + 226. New York and London: The Macmillan Company, 1927. Price: $3.00.* This book is really Claude Bernard's views on the methods of research and, as such, is of extraordinary value to all people doing research work. Though published more than sixty years ago, there is nothing better on the subject today and we are therefore indebted to the translator for making this book accessible to those who do not read French fluently.

"The art of investigation is the cornerstone of all the experimental sciences. If the facts used as a basis for reasoning are ill-established or erroneous, everything will crumble or be falsified; and it is thus that errors in scientific theories most often originate in errors of fact," p. 13.

"In scientific investigation, minutiae of method are of the highest importance. The happy choice of an animal, an instrument constructed in some special way, one reagent used instead of another, may often suffice to solve the most abstract and lofty questions. Every time that a new and reliable means of experimental analysis makes its appearance, we invariably see science make progress in the questions to which this means of analysis can be applied. On the contrary, a bad method or defective processes of research may cause the gravest errors, and may retard science by leading it astray. In a word, the greatest scientific truths are rooted in details of experimental investigation which form, as it were, the soil in which these truths develop," p. 14.

"Despite the important difference, which we have just pointed out, between the so-called sciences of observation and of experimentation, observers and experimenters still have the common and immediate object, in their investigations, of establishing and noting facts and phenomena as rigorously as possible, and with the help of the most appropriate means; they behave exactly as if they were dealing with two ordinary observations. In both cases, indeed, a fact is simply noted; the only difference is this,—as the fact which an experimenter must verify does not present itself to him naturally, he must make it appear, i. e., induce it, for a special reason and with a definite object. Hence we may say that an experiment is fundamentally just an observation induced with some object or other. In the experimental method, search for facts, i. e., investigation, is always accompanied by reasoning, so that experimenters usually make an experiment to control or verify the value of an experimental idea. Hence, in this case, the experiment is an observation induced with the object of control," p. 19.

"An experimenter, as we have already said, is a man inspired by a more or less probable but anticipated interpretation of observed phenomena, to devise experiments which, in the logical order of his anticipations, shall bring results serving as controls for his hypothesis or preconceived idea. To do this, an experimenter reflects, tries out, gropes, compares, contrives, so as to find the experimental conditions best suited to gain the end which he sets before him. Of necessity we experiment with a preconceived idea. An experimenter's mind must be active, i. e., must question nature, and put all manner of queries to it according to the various hypotheses which suggest themselves," p. 22.

"It has been said that the experimenter must force nature to unveil herself. Yes, the experimenter doubtless forces nature to unveil herself by attacking her with all manner of questions; he must never answer for her nor listen partially to her answers by taking, from the results of an experiment, only those which support or confirm his hypothesis. We shall see later that this is one of the great stumbling blocks of the experimental method. An experimenter, who clings to his preconceived idea and notes the results of his experiment only from this point of view, falls inevitably into error, because he fails to note what he has not foreseen and so makes a partial observation. An experimenter must not hold to his

idea, except as a means of inviting an answer from nature. But he must submit his idea to nature and be ready to abandon, to alter, or to supplant it, in accordance with what he learns from observing the phenomena which he has introduced.

"Two operations must therefore be considered in any experiment. The first consists in premeditating and bringing to pass the conditions of the experiment; the second consists in noting the results of the experiment. It is impossible to devise an experiment without a preconceived idea; devising an experiment, we said, is putting a question; we never conceive a question without an idea which invites an answer. I consider it, therefore, an absolute principle that experiments must always be devised in view of a preconceived idea, no matter if the idea be not very clear nor very well defined. As for noting the results of the experiment, which is itself only an induced observation, I posit it similarly as a principle that we must here, as always, observe without a preconceived idea," p. 23.

"People who condemn the use of hypotheses and of preconceived ideas in the experimental method make the mistake of confusing invention of an experiment with noting its results. We may truly say that the results of an experiment must be noted by a mind stripped of hypotheses and preconceived ideas. But we must beware of proscribing the use of hypotheses and of ideas when devising experiments or imagining means of observation. On the contrary, as we shall soon see, we must give free rein to our imagination; the idea is the essence of all reasoning and all invention. All progress depends on that. It cannot be smothered or driven away on the pretence that it may do harm; it must only be regulated and given a criterion, which is quite another matter.

"The true scientist is one whose work includes both experimental theory and experimental practice. (1) He notes a fact; (2) *à propos* of this fact, an idea is born in his mind; (3) in the light of this idea, he reasons, devises an experiment, imagines, and brings to pass its material conditions; (4) from this experiment, new phenomena result which must be observed, and so on and so forth. The mind of a scientist is always placed, as it were, between two observations: one which serves as starting point for reasoning, and the other which serves as conclusion.

"To make myself clearer, I have endeavored to separate the different operations of experimental reasoning. But when it all takes place at the same time in the head of a scientist, abandoning himself to investigation in a science as vague as medicine still is, then the results of observation are so entangled with the bases of experiment that it would be alike impossible and useless to try to dissociate, from their inextricable mingling, each one of these terms. It is enough to remember the principle that an *a priori* idea, or better, an hypothesis, is a stimulus to experiment, and that we let ourselves go with it freely, provided that we observe the results of our experiment rigorously and fully. If an hypothesis is not verified and disappears, the facts which it has enabled us to find are none the less acquired as indestructible materials for science.

"Observers and experimenters, then, correspond to different phases of experimental research. The observer does not reason, he notes; the experimenter, on the other hand, reasons and grounds himself on acquired facts, to imagine and induce rationally other facts. But though in theory and abstractly we may differentiate observers from experimenters, it seems impossible to separate them in practice, since we see that one and the same investigator, perforce, is alternately observer and experimenter," p. 24.

"We see, then, that the elements of the scientific method are interrelated. Facts are necessary materials; but their working up by experimental reasoning, i.e., by theory, is what establishes and really builds up science. Ideas, given form by facts, embody science. A scientific hypothesis is merely a scientific idea, preconceived or previsioned. A theory is merely a scientific idea controlled by experiment. Reasoning merely gives a form to our ideas, so that everything, first and last, leads back to an idea. The idea is what establishes, as we shall see, the starting point or the *primum movens* of all scientific reasoning, and it is also the goal in the mind's aspiration toward the unknown," p. 26.

"An anticipative idea or an hypothesis is, then, the necessary starting point for all experimental reasoning. Without it, we could not make any investigation at all nor learn anything; we could only pile up sterile observations. If we experimented without a pre-

conceived idea, we should move at random, but, on the other hand, as we have said elsewhere, if we observed with preconceived ideas, we should make bad observations and should risk taking our mental conceptions for reality," p. 32.

"Men who have excessive faith in their theories or ideas are not only ill prepared for making discoveries; they also make very poor observations. Of necessity, they observe with a preconceived idea, and when they devise an experiment, they can see, in its results, only a confirmation of their theory. In this way they distort observation and often neglect very important facts because they do not further their aim. This is what made us say elsewhere that we must never make experiments to confirm our ideas, but simply to control them; which means, in other terms, that one must accept the results of experiments as they come, with all their unexpectedness and irregularity," p. 38.

"Genius is revealed in a delicate feeling which foresees correctly the laws of natural phenomenon; but this we must never forget, that correctness of feeling and fertility of idea can be established and proved only by experiment," p. 43.

"A fact is nothing in itself, it has value only through the idea connected with it or through the proof it supplies. We have said elsewhere that, when one calls a new fact a discovery, the fact itself is not the discovery, but rather the new idea derived from it; in the same way, when a fact proves anything, the fact does not itself give the proof, but only the rational relation which it establishes between the phenomenon and its cause. This relation is the scientific truth which we now must discuss further," p. 53.

"We said above that experimenters, who see their ideas confirmed by an experiment, should still doubt and require a counterproof. Indeed, proof that a given condition always precedes or accompanies a phenomenon does not warrant concluding with certainty that a given condition is the immediate cause of the phenomenon. It must still be established that, when this condition is removed, the phenomenon will no longer appear. If we limited ourselves to the proof of presence alone, we might fall into error at any moment and believe in relations of cause and effect where there was nothing but simple coincidence. As we shall later see, coincidences form one of the most dangerous stumbling blocks encountered by experimental scientists in complex sciences like biology. It is the *post hoc, ergo propter hoc* of the doctors, into which we may very easily let ourselves be led, especially if the result of an experiment or an observation supports a preconceived idea.

"Counterproof, then, is a necessary and essential characteristic of the conclusion of experimental reasoning. It is the expression of philosophic doubt carried as far as possible. Counterproof decides whether the relation of cause to effect, which we seek in phenomena, has been found. To do this, it removes the accepted cause, to see if the effect persists, relying on that old and absolutely true adage: *sublata causa, tollitur effectus*. This is what we still call the *experimentum crucis*," p. 55.

"Only when a phenomenon includes conditions as yet undefined, can we compile statistics; we must learn, therefore, that we compile statistics only when we cannot possibly help it; for in my opinion statistics can never yield scientific truth, and therefore cannot establish any final scientific method," p. 137.

"One day, rabbits from the market were brought into my laboratory. They were put on the table where they uiinated, and I happened to observe that their urine was clear and acid. This fact struck me, because rabbits, which are herbivora, generally have turbid and alkaline urine; while on the other hand carnivora, as we know, have clear and acid urine. This observation of acidity in the rabbits' urine gave me an idea that these animals must be in the nutritional condition of carnivora. I assumed that they had probably not eaten for a long time, and that they had been transformed by fasting into veritable carnivorous animals, living on their own blood. Nothing was easier than to verify this preconceived idea or hypothesis by experiment. I gave the rabbits grass to eat; and a few hours later, their urine became turbid and alkaline. I then subjected them to fasting and after twenty-four hours or thirty-six at most, their urine again became clear and strongly acid; then after eating grass, their urine became alkaline again, etc. I repeated this very simple experiment a great many times, and always with the same result. I then repeated it on a horse, an herbivorous animal which also has turbid and alkaline urine. I found that fast-

ing, as in rabbits, produced prompt acidity of the urine, with such an increase in urea, that it spontaneously crystallizes at times in the cooled urine. As a result of my experiments, I thus reached the general proposition which then was still unknown, to wit, that all fasting animals feed on meat, so that herbivora then have urine like that of carnivora.

"We are here dealing with a very simple, particular fact which allows us to easily follow the evolution of experimental reasoning. When we see a phenomenon which we are in the habit of seeing, we must always ask ourselves what it is connected with, or putting it differently, what is its proximate cause; the answer or the idea, which presents itself to the mind, must then be submitted to experiment. When I saw the rabbits' acid urine, I instinctively asked myself what could be its cause. The experimental idea consisted in the connection, which my mind spontaneously made, between acidity of the rabbits' urine, and the state of fasting which I considered equivalent to a true flesh-eater's diet. The inductive reasoning which I implicitly went through was the following syllogism: the urine of carnivora is acid; now the rabbits before me have acid urine, therefore they are carnivora, i. e., fasting. This remained to be established by experiment.

"But to prove that my fasting rabbits were really carnivorous, a counterproof was required. A carnivorous rabbit had to be experimentally produced by feeding it with meat, so as to see if its urine would then be clear, as it was during fasting. So I had rabbits fed on cold boiled beef (which they eat very nicely when they are given nothing else). My expectation was again verified, and, as long as the animal diet was continued, the rabbits kept their clear and acid urine," p. 152.

"We have already said (p. 25) and we shall see further on, that in noting an observation we must never go beyond facts. But in making an experiment, it is different. I wish to show that hypotheses are indispensable, and that they are useful, therefore, precisely because they lead us outside of facts and carry science forward. The object of hypotheses is not only to make us try new experiments; they also often make us discover new facts which we should not have perceived without them. In the preceding examples, we saw that we can start from a particular fact and rise one by one to more general ideas, i. e., to a theory. But as we have just seen, we can also sometimes start with an hypothesis deduced from a theory. Though we are dealing in this case with reasoning logically deduced from a theory, we have an hypothesis that must still be verified by experiment. Indeed, theories are only an assembling of the earlier facts, on which our hypothesis rests, and cannot be used to demonstrate it experimentally. We said that, in this instance, we must not submit to the yoke of theories, and that keeping our mental independence is the best way to discover the truth. This is proved by the following examples," p. 162.

"Criticism of facts gives sciences their true individuality. All scientific criticism should explain facts rationally. If criticism is attributed, on the other hand, to personal feeling, science disappears; because such criticism rests on a criterion that can neither be proved nor conveyed as scientific truths should be. I have often heard physicians answer, when asked the reason for a diagnosis, "I do not know how I recognize such and such a case, but it is evident;" or when one asks them why they give certain remedies, they answer that they cannot exactly tell, and besides that they need not explain, since they are guided by their medical tact and intuition. It is easy to understand that physicians who reason in that way deny science. But we cannot too strongly protest against such ideas, which are bad, not only because they stifle every germ of science, but also because they especially encourage laziness, ignorance, and charlatanism. I entirely understand a physician's saying that he cannot always rationally account for what he is doing, and I accept his conclusion that medical science is still plunged in the shades of empiricism; but if he goes on to proclaim his medical tact or his intutition as a criterion which he then means to impose on others without further proof, that is wholly antiscientific," p. 193.

"In this connection it may be useful to recall, in a few words, the essential characteristics of the scientific method and to show how the ideas derived from it differ from systematic and doctrinal ideas. In the experimental method we never make experiments except to see or to prove, i. e., to control or verify. As a scientific method, the experimental method rests wholly on the verification of a scientific hypothesis. We obtain this verification with

the help, sometimes of a fresh observation (observational science), sometimes of an experiment (experimental science). In the experimental method, the hypothesis is a scientific idea that we submit to experiment. Scientific invention consists in the creation of fortunate and fertile hypotheses; these are suggested by the feeling or even the genius of the men of science who create them.

Wilder D. Bancroft.

Metallographie. *Die thermische Ausdehnung der Metalle und Legierungen. By A. Schulze. 26 × 18 cm. Berlin: Gebrüder Borntraeger, 1926. Price: 18.80 marks.* This book is part of the large text-book of Metallography edited by Dr. W. Guertler, and deals with the thermal expansion of metals and alloys. It opens with a general introduction to the subject and a consideration of the connection between this property on the one hand with the constitution, and on the other hand with the periodic system of the elements. The most important methods of measuring thermal expansion are reviewed.

The first main section is concerned with values obtained with metals and the most important of the non-metals. The author has drawn largely on the data contained in the tables of Landolt and Börnstein. A special reference is made by him to the investigations of Grüneisen and Goens on single crystals of eight elements, viz. zinc, cadmium, bismuth, antimony, tellurium, tin, sulphur and zirconium. None of these crystallise in the regular system, and the values obtained depend upon the orientation of the crystal. A special chapter deals with the expansion observed on melting.

In the second part the thermal expansion of alloys is considered, firstly in the crystalline state and secondly in the liquid state. These include cases of (1) complete immiscibility (2) limited miscibility, (3) complete miscibility and (4) alloys containing compounds. The author has not succeeded in establishing many relationships between thermal expansion and constitution. Very few alloy systems have been examined with sufficient completeness for this purpose. The best data available are those with alloys exhibiting complete miscibility. No systematic investigations of ternary alloy systems have been made. Fairly complete data are available for amalgams in the neighbourhood of the melting point. A series of liquid alloys has been systematically investigated by Bornemann and his co-workers, but as yet no very definite relationship has been established with constitution. The author states that his book is based upon information published down to the middle of 1926. The volume is printed with the same clearness of type and illustration that has distinguished the other parts of this great work on Metallography, and should be of considerable value.

H. C. H. Carpenter.

Gas and Gases. *By R. M. Caven. pp. vii + 256. New York: Henry Holt and Company, 1927. No. 119 of the Home University Library of Modern Knowledge.* This book is a popular exposition of the romance of the physics and chemistry of gases. It is divided into eight chapters, two of which, being on the gases of the atmosphere, constitute about one-third of the total number of pages. The Introduction consists of a very interestingly written account of the early history of gases, and although necessarily condensed to a few pages is a remarkably readable résumé of affairs chemical up to the time of Lavoisier. Chapter II, "The Gaseous State" is a simple yet rational account of the molecular theory and the kinetic theory of gases, the laws of Boyle and Charles, the diffusion of gases, and van der Waals' equation of state. Referring to the explanation of Gay-Lussac's law of combining volumes—page 32: "The explanation is that the atoms of hydrogen and chlorine go about in pairs, and that chemical combination is a change of partners. Just as during a ball an exchange of partners does not necessitate any change in the size of the ball-room, so the formation of hydrogen chloride, being an exchange of partners, does not result in any change of volume." Then follows a pictorial equation which introduces the reader to his first chemical equation.

Chapter III: "The Liquefaction of Gases": covers: the distinction between gases, vapors and mists or clouds; vapor pressure; the concept of an equilibrium; critical phenomena; methods of liquefaction, and uses of liquefied gases.

Chapters IV and V, devoted to The Gases of the Atmosphere, include the reasons why our earth has an atmosphere and the moon does not and the reasons why the composition of our air is as it is and not other gases is made clear. The rôle of carbon dioxide is dwelt upon at some length. Page 164, "The announcement towards the end of the war that it was proposed to use helium, on account of its lightness and non-inflammability, to fill airships, was received with scepticism by chemists, who had regarded this gas as chiefly confined, after its isolation, to vacuum tubes, on account of its rarity. Yet the proposal was serious, for there is a spring of natural gas at Bow Island, Alberta, Canada, which contains 0.36% of helium, and large amounts of this gas have now been obtained from this source. Moreover, experiments have shown that about twenty percent of hydrogen may be mixed with helium to lighten it, without producing an inflammable mixture." A still more impressive and complete picture of the extended use of helium in airships would have included the large scale operations of the separation of helium from natural gas in the United States, and its use to the extent of several million cubic feet in our airships, both rigid and non-rigid. Page 170, concerning the composition of the upper atmosphere: "Moreover, it is believed that another gas, known as *geocoronium*, which is lighter even than hydrogen, now makes its appearance, and that the outermost fringe of our atmosphere consists chiefly of this gas."

Chapter VI, "Useful Gases," considers oxygen, ozone, hydrogen, chlorine, nitrogen, carbon monoxide and carbon dioxide to be the principal gases of industrial application.

Chapter VII, "Gaseous Fuels" and Chapter VIII, "Combustion and Explosion of Gases," contain certain statements which perhaps are debatable, if one would be really critical. It is not to be expected, however, that any author could write as interestingly and accurately as Professor Caven has done without sacrificing a little of the rigorousness and exhaustive treatment that would be demanded of a purely scientific treatise. Only two minor typographical errors were noted by the reviewer, on page 104 "acide" is given for "acid" and on page 188, "ccurs" for "occurs".

This book is earnestly recommended not only for the interested layman and those who have been somewhat prepared by scientific news articles, but also for the student of chemistry who will find here a short and accurate résumé of gases and some of their fundamental properties.

J. H. Perry

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29, Rue Somi...
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THE COPPER NUMBER FOR GLUCOSE

BY CHESTER A. AMICK

Introduction

The copper number may be defined as the number of milligrams of copper precipitated as cuprous oxide from an alkaline solution of a copper salt by a unit quantity of any organic material. The determination of the copper number is a test made frequently by the carbohydrate chemist, wherein the carbohydrate is treated with alkaline copper oxide, held up usually by sodium potassium tartrate, although carbonates are used sometimes. The cuprous oxide which is precipitated by the reducing action of the carbohydrate is determined by weighing as such, oxidising to cupric oxide and weighing, or reducing to metallic copper and weighing. A shorter method is to oxidise the cuprous oxide in acidified iron alum solution and then titrate the ferrous salt with standard $KMnO_4$.

During the past twenty years, this method has been used by cellulose chemists in analysing certain degradation products of cellulose, particularly "so-called oxycellulose." The results which have been obtained have not been concordant and have led to considerable confusion concerning this so-called oxycellulose.

It was the original purpose of this investigation to determine the sources of error in the analytical procedure as applied to cellulose degradation products. The preliminary experiments, however, brought out three sources of error which indicated that cellulose could not be used in such an analytical study.

1. The cellulose adsorbs the alkali tartrate solution and the adsorbed material cannot be washed out entirely.

2. The acidified iron alum used to oxidise the cuprous oxide precipitated by the reducing action of the carbohydrate liberates the adsorbed tartrate, thus causing it to be present in the iron solution which is to be titrated with standard permanganate.

3. The presence of the iron salts accelerates the reduction of permanganate by the tartrates in acid solution, thereby causing unreliable results.

Because of these errors, it seemed logical to study a simpler carbohydrate such as glucose which is soluble in water. There are also four additional advantages in using glucose.

1. It has a known molecular weight.

2. Its molecular structure is well known, which should aid in establishing the course of the oxidation of the molecule.

3. This method has been used for its quantitative estimation for the past eighty years, and the analytical data gathered by numerous investigators should be of value in such a study.

4. Any conclusions based upon the study of glucose should be applicable, to some extent, to cellulose. Haworth and Hirst,[1] Hibbert,[2] Karrer,[3] Irvine,[4] and Gray[5] show a definite relation between glucose and cellulose, as they use 2,3,6 — tri-methyl glucose as a unit in building up their cellulose molecule.

The results which one obtains with glucose are also very discordant. The thirty-odd methods which are listed in the literature give values that vary as much as 1500 per cent in the amount of copper precipitated as cuprous oxide by 10 milligrams of glucose. To get concordant results by any method, it is necessary to use a flask or beaker having a definite surface area; the height of the solution in contact with the glass wall must be constant; the volume of the solution must be constant; the beaker must be placed at such a distance from the flame of the proper size as to bring the contents to boiling in a stated number of minutes, and this boiling must be continued for exactly the same number of minutes that the investigators used in preparing the empirical tables which accompany the method. Finally the solution must be filtered through an asbestos mat of practically non-varying thickness. Hot alkali dissolves this mat and a correction is necessary. Even with these precautions, the method recommended by the Association of Agricultural Chemists gives variations of two per cent from time to time,[6] due to variations in the atmospheric pressure and subsequent changes in the boiling points.

The copper number for glucose is much larger than the copper number for the same amount of cellulose. Schwalbe[7] who was the first to employ copper numbers in studying so-called oxycellulose used as his unit 100 grams of over-bleached cotton. A high copper number for such a sample would be, say 19300[8].

The copper number for a 10 mg. unit of glucose usually varies from 17 to 21. This would give a value for 100 grams of glucose of 170,000 to 210,000 as compared to the 19300 for cellulose. It is evident that 100 grams of glucose is too large for an experimental sample and a smaller unit, 10 mg., is used in all experiments in this paper unless otherwise stated.

It is possible to obtain a relationship between the copper number and the number of atoms of oxygen used by each molecule of glucose from the following equation.

$$2CuSO_4 + 4NaOH = 2Na_2SO_4 + 2CuO + H_2O$$
$$2CuO = Cu_2O + O$$
$$\text{glucose} + O = \text{glucose oxidation product, or glucose} + 2CuSO_4 + 4NaOH = 2Na_2SO_4 + Cu_2O + H_2O + \text{glucose oxidation product.}$$

[1] J. Chem. Soc., 119, 196 (1921).
[2] J. Ind. Eng. Chem., 13, 256, 334 (1921).
[3] Cellulose Chem., 2, 127 (1921).
[4] J. Chem. Soc., 123, 518-32 (1923); J. Soc. Chem. Ind., 41, 352-3R (1922); 44, 242 (1925).
[5] Ind. Eng. Chem., 18, 811 (1926).
[6] Quisumbing and Thomas: J. Am. Chem. Soc., 43, 1503-26 (1921); Trophagen and Cobleigh: J. Am. Chem. Soc. 21, 369 (1899); Rosenkranz: Z. Vereins deutsch. Zuckerindustrie, 61, 426 (1911).
[7] Ber., 40, 1347 (1907).
[8] Matthews: "Bleaching", 487.

For a 10 mg. sample, a copper number of 7.063 is equivalent to one atom of oxygen per molecule of glucose. Thus, the value given above (17—21) indicates that each molecule of glucose usually combines with two and a half to three atoms of oxygen.

It will be shown in this paper that: (1) Soxhlet's conclusions in 1880 that "the use of alkaline copper solutions in estimating glucose are valueless" are confirmed; (2) the amount of oxygen used is dependent upon the alkalinity of the solution; (3) the change from one atom of oxygen used to two, or from two to three, etc., is gradual, indicating that the formation of gluconic acid or saccharic acid is not a necessary step in the oxidation; (4) solutions made alkaline by carbonates give higher copper numbers than those using free alkali; (5) the results are in agreement with the theories proposed by Nef and his school for the formation, by reducing sugars in alkaline solutions, of enediols and subsequent fission; (6) the reducing action of sugars is *not* due to carboxyl formation from the carbonyl group as is commonly supposed; (7) the oxidation of the carbonyl group to the carboxyl stabilizes the molecule; (8) since the copper number depends upon the alkalinity, conditions may be chosen which give any concordant results which one desires, but the results so obtained have no significance; (9) the alkaline tartrate solution is adsorbed by the asbestos mat or filter paper and cannot be removed completely by washing; (10) the volumetric method of Bertrand is inaccurate, because the iron salts used in the process catalyse the oxidation of the adsorbed tartrates by permanganate; (the errors are much greater where this method is adapted to the determination of the copper number of cellulose); (11) from an alkaline copper oxide solution the precipitated cuprous oxide can be estimated without filtering from the reaction mixture by using phospho-molybdic reagent in the cold; under certain conditions by using iron salts with sodium fluoride in the cold; and under certain conditions, by using iron salts with sodium pyrophosphate in the cold; (12) the alkaline copper oxide is a stronger oxidising agent than Fehlings solution.

Estimation of the Copper Number of Glucose Origin

Although the ancient Egyptians[1] knew that if honey was boiled with vinegar and *verdigris* a brown precipitate was formed, and Vogel[2] and Buchner[3] found that certain sugars, just as honey, would produce the same effect, it was Trommer[4] who first realized that glucose (grape sugar) could be differentiated from sucrose by this reaction. Baumé[5] attributed the brown precipitate to the phlogiston of the acetic acid uniting with the verdigris to form metallic copper, but Vogel and Trommer found it was due to cuprous oxide which had been formed from the copper salt present. Trommer used an alkaline solution of copper sulphate which gave a precipitate of black copper oxide as well

[1] Mellor: "Treatise on Inorganical and Theoretical Chemistry," **3**, 120 (1923).
[2] Schweigger's J., **13**, 162 (1815).
[3] Schweigger's J., **14**, 224 (1815).
[4] Ann., **39**, 360 (1841).
[5] Elemens de pharmacie théorique et practique (1762).

as the red cuprous oxide. Barreswil[1] found that a neutral potassium tartrate prevented this black copper oxide from precipitating and worked out the first analytical tables for sugar analysis. This analytical method, however, was unsatisfactory, and Fehling[2] after several years of study, announced the conditions[3] which have been largely followed up to the present time.

Fehling started with 40 grams of copper sulphate and then added Rochelle salts and alkali until no black copper oxide was precipitated on heating. This gave a total solution of 1154.4 cc., which was recalculated by Tollens and Rodewald[4] on the basis of one liter as follows:

A.	Copper sulphate-hydrated	34.639 gms.
B.	Seignette Salts	173.0 gms.
	Sodium hydroxide	60.0 gms.

Fehling had mixed the solution ready for use, but Soxhlet[5] later found that copper oxide precipitated on standing. He recommended that the copper sulphate be made up to one-half liter, the Seignette salts and alkali (52 gms. NaOH for glucose) be made up to one-half liter, and equal parts used as needed, a practice which has continued to the present time. Thus the solution consists of two parts, A and B, and will be referred to as such in this paper. A third part, C, is the determination of the cuprous oxide precipitated by the reducing action of the carbohydrate from this alkaline copper solution. This is usually accomplished by one of three methods:

1. Weighed as cuprous oxide.
2. Reduced to metallic copper and weighed.
3. Oxidized to cupric oxide and weighed.

A shorter method is to dissolve the cuprous oxide in acidified iron alum solution, and then titrate the ferrous salt with standard potassium permanganate.

Unfortunately, there are several substances which may be used in part B to prevent the precipitation of black copper oxide, such as glycerine,[6] carbonates,[7] citrates,[8] or ammonia.[9] It was inevitable that these substances should be discovered, and the literature flooded with new methods for the estimation of reducing sugars. The results obtained by these various methods are very discordant, the values for the copper number of 10 milligrams of glucose varying as much as 1500 per cent, as is indicated in Table I.

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[1] J. Pharmacie, (3) **6**, 301 (1844).
[2] Ann., **72**, 106 (1849).
[3] Fehling: Ann., **106**, 75 (1858).
[4] Ber., **11**, 2076 (1878).
[5] Soxhlet: Chem. Centralblatt, **1878**, 218.
[6] Ruosz: Chem. Abs., **13**, 2771 (1919); Löwe: Z. analyt. Chem., **9**, 20 (1870); **10**, 453 (1871).
[7] Soldiani: Gazz., **6**, 322 (1776); Z. Vereins deutsch. Rüben Zückerindustrie, **1887**, 145; **1888**, 722; **1889**, 933; **1890**, 19, 51.
[8] Benedict: J. Biol. Chem., **64**, 207 (1925).
[9] Pavy: "Physiology of Carbohydrates," 71 (1894).

TABLE I

10 mg. glucose is equivalent to A mg. copper

Author	A	Author	A
Violette[1]	17.62	Benedict[6]	24.10
Hoppe-Seyler[2]	17.63	Munsen and Walker[7]	21.30
Possoz[3]	1.80	Brown, Morris and Millar[8]	20.60
Krocher[4]	2.40	Quisumbing and Thomas[9]	21.42
Soldiani and Ost[5]	32.30	Bertrand[10]	20.40

The Mechanism of Fehling Solution

It has already been mentioned that Barreswil added neutral potassium tartrate to the alkaline copper solution in order that the black copper oxide would not be precipitated. Fehling replaced the potassium tartrate with Seignette salts, a sodium-potassium-tartrate for the same purpose. It was not indicated that any compound was formed between the copper and the tartrate.

Küster,[11] Masson and Steele,[12] Kahlenberg[13] and others[14] have studied the properties of Fehling solution. Its electrical behavior indicates that the copper is either combined in the anion or is colloidal, as it goes to the anode when a current is passed. On the compound basis, various NaCu tartrates have been postulated, but probably only $CuNa_2C_4H_2O_3 . 2H_2O$ has been isolated.[15]

Hugo Schiff[16] found that if hot concentrated solutions of Rochelle salts and copper sulphate are mixed, a compound of the formula $C_4H_4Cu_2O_5$ separated. He found that this dry powder was soluble in alkali, and that only a little cuprous oxide separated after boiling. Schiff used this dry powder to prepare fresh Fehling solution, which he utilized in estimating reducing sugars. Masson and Steele have found that this copper tartrate combines with NaOH in the molar ratio 1 — 1.25 to give the deep blue Fehling solution which is neutral. Additional NaOH makes the solution alkaline. KOH combines with

[1] "Dosage du Sucre" (1868).
[2] Wiley: "Agricultural Analysis," 128 (1897); Horton: J. Anal. Chem., 4, 372 (1890).
[3] Wiley: "Agricultural Analysis," 129 (1897); Horton: J. Anal. Chem., 4, 374 (1890).
[4] "Leitfaden qual. quant. chem. Analyse, 3 Aufl, 460 (1871).
[5] Ber., **23**, 1035 (1890); Chem. Ztg., **19**, 1784 (1890).
[6] J. Biol. Chem., **3**, 101-7 (1907).
[7] J. Am. Chem. Soc., **28**, 663 (1906); **29**, 541 (1907).
[8] J. Chem. Soc., **71**, 94 (1897).
[9] J. Am. Chem. Soc., **43**, 1503-26 (1921).
[10] Bull., **35**, 1285 (1906).
[11] Z. Elektrochem., **4**, 105-13 (1897): B. C. A., **74**, (11) 204 (1898).
[12] J. Chem. Soc., 75, 725 (1899).
[13] Kahlenberg: Z. physik. Chem., **17**, 586 (1895).
[14] Bullnheimer-Seitz. Ber., **32**, 2347: **33**, 817 (1900); Marre: Centralblatt, 1905, (2), 615. Byk: Z. physik. Chem., **61**, 5 (1908). Grossman-Löb: Centralblatt, 1908, II, 1996.
[15] Holleman-Walker: "Textbook of Organic Chemistry," 212 (1924); Meyer and Jacobson: "Lehrbuch der organischen chemie," 673 (1909-13).
[16] Ann., **112**, 368 (1859).

copper tartrate in the same proportion to give a neutral solution. From this fact, these authors assumed that the copper was present in Fehling solution as $Na_3C_{12}H_7Cu_4O_{18}$ but did not isolate this compound.

In this work the solutions were examined by the ultra-microscope and no suspensions were observed. Three collodion tubes were prepared, the solution placed in them and they were then stood in distilled water. The color of the solution appeared in the water 15-30 minutes later and the tubes were dissolved after 10 or 12 hours, due probably to the action of the alkali in the Fehling solution. Another sample was treated with hydrogen sulphide and a black precipitate of CuS was obtained. Brown and Mathers[1] used a solution resembling Fehling's to plate copper on iron, and this behavior, together with the three preceding tests indicates the presence of dissolved and not of colloidal copper oxide.

Staud and Gray Method of estimating the Copper Number

This method[2] was the first one to be studied in the preparation of this paper. It employs Fehling solution, but determines the precipitated cuprous oxide by dissolving it in acidified iron alum (ferric salt) and titrating the ferrous salts with standard potassium permanganate, a method first used by Mohr[3] and later by Bertrand.[4]

Materials

A. Copper Sulphate Solution. 68.5 grams of recrystallized $CuSO_4.5H_2O$ were dissolved in water and made up to 1 liter.

Quisumbing[5] recommends using a concentrated copper sulphate solution, determining the copper electrolytically in a definite quantity of the solution, and then adding sufficient to give the desired amount. As will be shown later, the difficulties in copper number determinations probably do not hinge upon such a delicate adjustment of the copper content.

B. Alkaline Tartrate Solution. 346 grams of potassium sodium tartrate (Kahlbaum or Baker's C. P.) which have been recrystallized twice from distilled water and dried at room temperature were dissolved in half a liter of distilled water. 100 grams of Sodium Hydroxide were added and the solution diluted to 1 liter. The sodium hydroxide should be freed from carbonates by making up a saturated solution and letting stand for 10 days or longer. The clear solution is then decanted off, its strength determined, and sufficient to make 100 grams of NaOH added to the Rochelle salts solution.

C. Ferric Ammonium Alum Solution. 100 grams of this salt $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$ are placed in half a liter of distilled water and 140 cc. of concentrated sulphuric acid added. The solution is made up to one liter.

D. Potassium Permanganate Solution. 5 grams of this material are dissolved in a liter of water, boiled for 10 minutes, and left for a day before

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[1] J. Phys. Chem., **10**, 39 (1906).
[2] Ind. Eng. Chem., **17**, 741 (1925).
[3] Mohr: Z. anal. Chem., **12**, 296, 373 (1873).
[4] Bertrand: Bull., **35**, 1285 (1906).
[5] Quisumbing: J. Am. Chem. Soc., **43**, 1503-26 (1921).

filtering through an asbestos mat in a Gooch filter. The filtrate is then diluted to about four liters, and standardized with hot sodium oxalate containing 10 cc. of 1 – 1 H_2SO_4. This gives a permanganate solution about N/25, one cc. of which will be equivalent to about 2.5 milligrams of copper.

E. The glucose (dextrose or d-glucose) was made by Mulford of Philadelphia. It contained 8.92 per cent moisture which was determined by heating two grams of glucose in a platinum dish at 60° in an evacuated Mojonnier Bros. muffle under a reduced pressure of seven inches of mercury for three hours. The temperature was then raised to 70° and the heating continued until the dish and its contents acquired a constant weight. The amount required to make 0.4 grams of the anhydrous glucose was then dissolved in distilled water and made up to 200 cc. Five cc. of this solution, containing 10 milligrams, were used in each of the following experiments unless otherwise indicated.

Procedure

A one-liter balloon flask (Pyrex) was placed in an automatic water bath to such depth that the water outside was higher than the contents of the flask. (This size flask was used because it was expected later to determine the copper number for some cellulose materials.)

In a 200 cc. Pyrex beaker, 20 cc. of the copper sulphate solution and 30 cc. of the alkaline tartrate solution were diluted with 95 cc. of distilled water. This was heated to 95°C., (it bumped, and boiled over if heated to boiling) and then poured into the balloon flask. Five cc. of the glucose solution were then added and a small watch glass was placed over the balloon flask, which was then heated thirty minutes. At the end of the heating period, the flask was removed, and the contents filtered on a Buchner funnel through two hardened filters,[1] washed with a liter of hot water and finally with enough cold water to cool the apparatus to room temperature. (Usually two liters were sufficient.) The last of the wash water was tested with phenolphthalein[2] and a blank was assumed to indicate the absence of any alkaline tartrate solution.

The funnel was then transferred to another filter flask, 25 cc. of the acidified iron alum solution added, the filter then washed with water, with 50 cc. of 2 N sulphuric acid, and again with water. The last of the wash water was tested with potassium ferrocyanide, which would indicate both iron and copper salts. A negative test was always obtained. The copper number of the ferric alum and sulphuric acid was determined and subtracted from the value for the sample.

Errors from Study of the Staud and Gray Method

1. These investigators found a slight auto-reduction of the Fehling solution. This was confirmed when the method was carried out as suggested by these investigators. This auto-reduction can be completely eliminated, how-

[1] Carl Schleicher and Schüll, No. 575, 9 cm.

[2] The fact that there is no positive test here with phenolphthalein does not eliminate the presence of tartrates because the solution contains 3.73 grams of tartrates for each gram of alkali.

ever, if water absolutely free from organic[1] material is used in the preparation of the solution, and a watch glass[2] or glass-fitted reflux condenser is used instead of one fitted with cork. The solvent action of the steam on cork gives a material which will reduce Fehling's solution.

2. It was noticed that after the Fehling solution containing the cuprous oxide precipitated by the reducing action of the carbohydrate had been poured on the filters, the subsequent washing never removed all the blue color. Washing with three liters of boiling water and a similar amount of cold water failed to remove all the color. But the addition of the acidified ferric alum solution *did* remove the color. This indicated that some of the Fehling solution was present in the final titration mixture.

3. Tartrates reduce permanganate. The end-point obtained by such titrations was not satisfactory, because it faded quickly. If the solution was warmed, the end-point was not sharp, and was less stable than in the cold. While this did not necessarily prevent concordant results from being obtained, providing the time of the titration, the temperature of the solution, and its volume were kept constant, it was evident that some other material was assisting in reducing the permanganate. Five grams of Rochelle salts were dissolved in 25 cc. of distilled water, 5 cc. 1:1 H_2SO_4 added and N/25 $KMnO_4$ added, drop by drop. The permanganate was reduced practically instantaneously in the cold. If the Rochelle salt solution was heated, it reduced $KMnO_4$ nearly as rapidly as it was run in from a burette.

One half gram of Rochelle salts was then dissolved in 25 cc. of H_2O and 5 cc. 1:1 H_2SO_4 added, and the solution diluted to 100 cc. This solution reduced $KMnO_4$ slowly but steadily. A second solution was prepared as the last one, except that 25 cc. of the acidified iron alum solution was added in place of 25 cc. of water. This solution reduced the standard permanganate rapidly. To insure that the acidity was not responsible for this accelerated reduction, two more solutions were prepared, each containing one-half gram of Rochelle salt, and 50 cc. of H_2O. To one was again added 25 cc. of the acidified iron alum solution, to the other 25 cc. of water containing 140 cc. of H_2SO_4 per liter (the same concentration of acid as is present in the iron alum solution). Again the solution containing the iron alum reduced the permanganate much more rapidly than the other one.

The acceleration of reactions in the presence of iron salts is not a recent discovery. In 1894, Fenton[3] observed that tartaric acid dissolved in three per cent hydrogen peroxide, is rapidly oxidised if a trace of ferrous sulphate be added. Similar observations were also made by him in the case of many hydroxy acids and poly-atomic alcohols. Cross, Bevan and Smith,[4] as well

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[1] Water can be freed from organic material by distilling in the presence of phosphoric acid and permanganate.

[2] If a watch glass is used, small additions of distilled water must be made from time to time to replace the water which escapes by evaporation.

[3] J. Chem. Soc., **65**, 899 (1894); **75**, 1 (1899); **77**, 69, 1294 (1900).

[4] Cross, Bevan and Smith: J. Chem. Soc., **73**, 463.

as Morrell and Crofts[1] have applied Fenton's reaction to the carbohydrates and have determined the character of some of the oxidation products formed.

Fenton supposed that the ferrous salt had a specific effect in the reactions under consideration, whereas Ruff[2] attributed the catalytic effect to the presence of the ferric salt. Spoehr[3] found that the reaction proceeded equally well in the presence of traces of a ferric or ferrous salt. He stated. "whether a ferrous or ferric salt be used, the iron in solution in hydrogen peroxide is always in the "*ferrous*" condition as long as there is simultaneously present a reducible substance, as sugar, etc. As soon as the latter is consumed, the iron is oxidised to the ferric condition."

This statement is not supported by the facts. If an acidified tartrate solution has ferric ions (ferric alum) added, it will reduce permanganate rapidly. If however, a substance is added which forms a complex with the ferric ions, but does not with the ferrous ions, the acidified tartrate solution does not reduce permanganate more rapidly than when no iron salts are added. This proves that the ferric ions, alone, act as the catalyst.

Schilow[4] in discussing the reduction of $KMnO_4$ by tartaric acid as an induced reaction, states, "Kessler[5] was the first to observe the effect of traces of an iron salt on the oxidation of tartaric acid by potassium permanganate. He further observed that zinc chloride, arsenious acid, antimony oxide, sulphuric acid, and potassium ferrocyanide affected the rate of this oxidation, as well as manganous salts. Kessler described this type of reaction as a "coupled" or "induced" reaction. The reagent which took part in both reactions he defined as the actor; that which entered only in the primary reaction was the inductor, and the reagent which entered only in the secondary reaction, he defined as the acceptor."

Recently Dhar and Mittra[6] have shown that sugars, starch, and alcohol can be oxidized by atmospheric oxygen in the presence of inductors such as sodium thiosulphate and ferrous hydroxide. Spoehr[7] and Spoehr and Smith[8] claim to have oxidized glucose by atmospheric oxygen by means of sodium-ferri-pyrophosphates. There is something queer about this and the experiments should be repeated to see what has been omitted from the account.

4. Another instance of the probable effect of iron salts in oxidations is in the determination of oxygen consumed in water analysis. Woodman[9] claims that the oxidation of organic material by permanganate gives only relative amounts, and these only when the various samples compared are practically

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[1] Morrell and Crofts: J. Chem. Soc., **75**, 786; 77, 1219; **81**, 666; **83**, 1284; **87**, 280.
[2] Ruff: B., **31**, 1573 (1098); **32**, 550, 3672 (1899); **33** 1798 (1900); **34**, 1362 (1901)
[3] Spoehr: Am. Chem J., **43**, 248 (1910).
[4] Schilow: Z. physik. Chem., **42**, 660 (1902); **46**, 777 (1903).
[5] Pogg. Ann., **95**, 224 (1853); **96**, 332 (1855); **113**, 142 (1861); **118**, 60 (1863); **119**, 218 (1863).
[6] J. Phys. Chem., **29**, 376, 739 (1925).
[7] J. Am. Chem. Soc., **46**, 1494 (1924).
[8] J. Am. Chem. Soc., **48**, 241 (1926).
[9] J. Am. Chem. Soc., **20**, 497 (1898).

identical in composition. Some "sewage-free" waters give high "oxygen consumed" results. He further states that the oxidation by permanganate varies with:

1. The nature of the organic matter.
2. The manner in which the determination is made.

From what we have just seen concerning the influence of iron salts in inducing an oxidation of organic materials by permanganate, the presence of a little iron in the water may alter the results considerably. So far as the experiments made at Cornell are concerned, there is no proof of the ferric ion acting as anything more than a catalyst.

Other Errors in the Determination of the Copper Number for Glucose

The effect of iron salts on the oxidation of tartrates precludes their use for accurate work, where the reduction is due to the glucose molecule alone. However, iron salts may not prevent the obtaining of concordant results, providing the limitations are kept in mind, and that all conditions are maintained absolutely constant. In Bertrand's[1] method for estimating the copper number of various sugars, this same reaction is one of the causes for error. Davis and Daisch[2] failed to get results to check closer than 1.5 per cent. These same investigators also found that it was impossible to use a gravimetric method in estimating reducing sugars, as the hot alkaline tartrate solution dissolves the asbestos mat (or filter paper) on which it is filtered. They found that the method of Brown, Morris and Millar[3] gave poor checks, due to variations in the asbestos layer, thicker layers giving larger variations. Others have had difficulty in using asbestos mats for filtering purposes, a method originally proposed by Soxhlet.[4]

Thus Tollens and Rodewald,[5] Nihoul,[6] and Gaud[7] felt that the asbestos mat was better than filter paper, because there was less chance of fine cuprous oxide going through, and "there was less chance for the precipitated cuprous oxide to redissolve in a narrow asbestos mat" (probably by oxidation first and then solution of the black copper oxide). But Killing,[8] Maercker,[9] and Grünhut[10] found that filter papers were far superior to asbestos mats, and that certain kinds of asbestos are greatly dissolved by hot alkali. Even glass wool is attacked by the hot alkali.

The gravimetric methods give too high results, as some cupric oxide is adsorbed by the cuprous oxide. This may be shown microscopically, since cuprous oxide is oxidized by ferric alum to cupric sulphate while cupric oxide

[1] Bull., **35**, 1285 (1906).
[2] J. Agricultural Sci., **5**, 437 (1913).
[3] J. Chem. Soc., **71**, I, 94 (1897).
[4] J. prakt. Chem., (2) **21**, 277-317 (1880).
[5] Ber., **11**, 2076 (1878).
[6] Chem. Ztg., **17**, 500 (1893); **18**, 881 (1894).
[7] Compt. rend., **119**, 478-79 (1894).
[8] Z. angew. Chem., **1894**, 431-33.
[9] Handbuch Spiritus-fabrikation, 4, Aufl. 85.
[10] Chem. Ztg., **18**, 447 (1894).

is not. This error, however, may not prevent the obtaining of concordant results. This is not the only source of error in the gravimetric methods; Sherwood and Wiley[1] find that the weighing of cuprous oxide directly gives too high results, due to the organic impurities that are also carried down. Brunner[2] says that too little cuprous oxide is obtained because some goes through the filter. Ulbricht[3] claims that the reduction of cuprous oxide in a current of hydrogen gives too high results because the metallic copper adsorbs hydrogen. Allihn[4] takes exception to Brunner's statement and shows from the experiments of Graham[5] that the amount of hydrogen adsorbed is insignificant.

The volumetric methods employing iron alum and standard permanganate also give too high results because of the adsorption of Rochelle salts from the Fehling solution by the asbestos mat, and their subsequent liberation by the acidified iron alum solution.

Elimination of Tartrates from Alkaline Copper Solutions

The tartrates were now eliminated from alkaline copper solutions and analysis made by adding copper sulphate to glucose, heating in a water bath, and then adding alkali. The alkali cannot be added to the glucose before the copper sulphate, as it decomposes glucose into products which have less reducing power. The glucose oxidation products are oxidized slowly by permanganate, more rapidly in the presence of iron salts, but if phospho-molybdic reagent is used in place of the iron alum, the cuprous oxide which is precipitated can be determined by titrating with standard permanganate in the cold, and it is unnecessary to filter. The experimental evidence follows:

A comparison of the oxidising power of Fehling solution and alkaline copper oxide is interesting. If the copper oxide goes into true solution with the Rochelle salts, the concentration of copper ion must be less then if the solution is saturated with respect to copper ion. Therefore, the oxidising power of this copper must be less than that of an alkaline colloidal solution of copper oxide. However, the latter solution may require more time to complete the oxidation.

To clear up the preceding question, three experiments were performed:

1. To a sealing-off tube were added two grams of granular black copper oxide (copper oxide wire), the tube nearly filled with the alkaline Rochelle salt solution (B of Fehling), the tube then sealed-off, and set away.

2. A second tube was filled in the same manner, except that fine cupric oxide was used.

3. The third tube was filled nearly full of Fehling solution, sealed-off and then set away.

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[1] U. S. Bureau of Chemistry, Bull. **108**, 120.
[2] Z. anal. Chem., **11**, 32 (1872).
[3] Chem. Centralblatt, **75**, 392 (1878).
[4] J. prakt. Chem., (2) **22**, 66 (1880).
[5] Ann., Suppl., **5**, 66 (1867). See also Lietzenmayer: Ber., **11**, 306 (1878).

If the copper oxide dissolved in the alkaline-tartrate solution, it would be indicated by the intense blue of Fehling solution and would indicate that the concentration of copper ions was less in true solution. This actually happened in less than twenty-four hours, both with the granular and the fine copper oxide. If the copper oxide were merely in suspension in a Fehling solution, then, on long standing, some black copper oxide would separate just as the case with alkaline chromic oxide. This was to be shown by the third experiment. However, after standing ten weeks there was no indication of copper oxide settling out.

Materials for Alkaline Copper Solutions.

A. Copper sulphate — $5H_2O$. 249.90 grams of selected crystals (one gram-mole) were dissolved in water and diluted to one liter. One cc. of this solution contained 63.57 mg. of copper or a copper number equivalent to 9 atoms of oxygen (1 gram atom of oxygen has a copper number of 7.068).

B. Sodium hydroxide. The strength of the carbonate-free alkali which had been prepared for the Fehling solution (see p. 1446) was determined by titrating with standard hydrochloric acid, using methyl orange as indicator. Enough of this alkali was then used to give 80 grams NaOH per liter, which gave a 2 N—or 2 M—solution. One cc. of the alkali would just convert one cc. of the standard copper solution to cupric oxide or hydroxide.

C. Phospho-molybdic reagent.[1] 100 grams of sodium molybdate (Baker's C. P.) were dissolved in 500 cc. of distilled water and then 75 cc. of phosphoric acid (85%), 275 cc. of concentrated sulphuric acid and sufficient water to make a total volume of 1750 cc. were added in the order named. This solution may be filtered if necessary and stored in a convenient bottle. If the order of addition is varied, a yellow precipitate of sodium-phospho-molybdate is likely to occur.

D. and E. Glucose and Iron alum solutions respectively were prepared as before (pp. 1446-1447).

Procedure: A 500 cc. Pyrex beaker (tall form) was filled about half full of water to serve as a water bath. Two Pyrex test tubes, (8″ × 1″) were then placed in the beaker and secured by means of two No. 12 cork stoppers placed between the test tubes and the beaker sides, so that the bottoms of the test tubes rested about half an inch from the bottom of the beaker. This tended to prevent super-heating and also made possible the use of a small cover glass to serve as a condenser, since the test-tubes were supported in an upright position. When ready to make a determination, 10 cc. of distilled water were added to each of the test tubes, then 5 cc. of glucose solution containing 10 milligrams of (anhydrous) glucose and 1 cc. of the standard copper sulphate solution. The tubes were then placed in position as previously indicated, and heated in the water bath for five minutes. It had previously been found by Kjeldahl, confirmed by Quisumbing and Thomas and also in this work that

[1] Brode: "Determination of the Copper Number." Report of the committee of the Cellulose Division of the Am. Chem. Society, Philadelphia (1926).

(see p. 1462 for the experimental evidence) the oxygen in the atmosphere oxidized some of the cuprous oxide back to cupric oxide. Therefore, after the alkali was added, a current of nitrogen washed by a train of pyrogallol and distilled water was led in to replace any oxygen, the cover-glass replaced, and the heating continued for the time of the experiment. This was found to be complete in ten to twelve minutes, but no noticeable change occurred if continued longer. The tubes were then removed and without undue agitation, or removing the cover-glass placed in a bath of ice water and permitted to cool to room temperature (22°–25°C). Twenty-five cc. of the acidified iron alum solution were then added, the whole transferred to a 500 cc. Pyrex beaker, diluted to 200 cc., let stand five minutes, and then titrated with standard permanganate. Since the amount of glucose to be oxidized is unknown, more copper sulphate and sodium hydroxide should be added than is actually necessary. This precludes estimation by any of the gravimetric methods and consequently suggests the use of iron alum, since no tartrates are present to interfere. The following data indicate the course of the investigation to obtain an analytical method which would make filtration unnecessary. They were obtained by using Pyrex test tubes 10 mm. × 150 mm. (⅜″ × 6″) which were not covered.

TABLE II

1 cc. NaOH, 1 cc. $CuSO_4.5H_2O$ and 5 cc. glucose (0.01 gm.) added in the order given.

Time of heating	Temp. of heating	Excess NaOH	Permanganate used	Copper in milligrams
16	99	None	1.9	10.20
16	99	”	2.2	11.81
15	99	”	2.5	13.42
46	99	”	2.75	14.77
55	99	”	2.45	13.15
70	99	”	2.65	14.23

TABLE III

2 cc. NaOH, 1 cc. $CuSO_4.5H_2O$ and 5 cc. glucose (0.01 gm.)

Time of heating	Temp. of heating	Excess NaOH*	Permanganate used	Copper in milligrams
16	99	About 1%	3.00	16.11
22	99	” ”	2.90	15.57
30	99	” ½%**	2.25	12.08
85	99	” ” ”	2.20	11.81

*Solution contains 1% alkali, or
**one half.

The precipitate of cuprous oxide in the last four experiments had a brighter red color and filtered better than those where the theoretical amount of NaOH was used. The last two in Table III were diluted with 5 cc. water before placing in the bath.

TABLE IV

3 cc. NaOH, 1 cc. $CuSO_4.5H_2O$ and 5 cc. glucose (0.01 gm.) added in the order given.

Time of heating	Temp. of heating	NaOH Solution	Permanganate used	Copper in milligrams
30	99	2%	3.00	16.11
30	99	2%	3.20	17.18
30	99	2%	3.25	17.45
30	99	2%	2.75-3.20	(16.11)?*

*The end-point is so uncertain that it changed from 2.75-3.20 in the course of fifteen or twenty seconds. None of these determinations have yielded a satisfactory end-point thus far.

The results in the foregoing experiments were not concordant, yet they seemed to indicate an increase in copper number as the concentration of alkali increased.

Benedict[1] stated that glucose boiled with 10 per cent potassium hydroxide for a few minutes did not reduce Fehling solution. He stated that the glucose had been "completely oxidized" by heating with the alkali. In order to determine the effect of the 1% alkali that we had been using, 5 cc. of the glucose solution (0.01 gm.) was heated for 2½ hours with 2 cc. 2N.NaOH and 10 cc. of water. At the end of each hour, the evaporated water was replenished (about 2 cc.) so that the concentration remained practically at 1%. Then 1 cc. of the copper sulphate solution was added and the heating continued for 20 minutes. Each sample was filtered through an asbestos mat in a Gooch filter, and both the residue and the filtrate, separately oxidized with ferric alum, and then titrated with permanganate. It was observed here that the residue gave a *sharp* end-point and the filtrate gave a *fading* end-point. Table V gives the results of this treatment. Table VI is for comparison with Table V. Here the same quantities were used as in Table V, but the glucose was not heated with alkali before the copper sulphate was added. In Table VII the glucose was not heated with alkali before the copper sulphate was added, the same quantities were added, but the solution was *not filtered* as in Tables V and VI. The ferric alum was here added to the cold solution.

TABLE V

2 cc. NaOH, 0.01 gm. glucose, and 10 cc. H_2O heated for 2½ hours before 1 cc. $CuSO_4.5H_2O$ was added, and the heating continued for twenty minutes.

Temp. 99°C.

Time of heating	$KMnO_4$ for Residue	Cu. in Mg.	$KMnO_4$ filtrate	Cu in Mg	Total copper
19	0.25	1.34	——	——	——
28	0.30	1.61	0.20	1.07	2.68
38	0.25	1.34	0.20	1.07	2.41
48	0.25	1.34	0.15	0.80	2.14

[1] Benedict: J. Biol. Chem., 3, 101-7 (1907).

TABLE VI

2 cc. NaOH, 1 cc. $CuSO_4.5H_2O$, 0.01 gm. glucose and 10 cc. H_2O heated in the water bath for twenty minutes. Temp. 99°C.

Time of heating	$KMnO_4$ for Residue	Cu. in Mg.	$KMnO_4$ for filtrate	Cu in Mg	Total copper
20	1.40	7.51	0.30	1.61	9.12
20	1.2	6.44	0.35	1.87	8.31
42	1.25	6.71	0.25	1.34	8.05
55	1.75	9.39	0.30	1.61	11.00

TABLE VII

2 cc. NaOH, 1 cc. $CuSO_4.5H_2O$, 0.01 gm. glucose and 10 cc. H_2O heated in the water bath for twenty minutes, and the ferric alum added without filtering. Temp. 99°C.

Time of heating	Permanganate used	Copper in milligrams	Time of heating	Permanganate used	Copper in milligrams
20	1.30	6.98	27	1.95	10.47
22	2.0	10.74	29	1.65	8.86
24	2.05	11.01	23	2.0	10.74
26	2.05	11.01	25	1.8	9.66
23	1.5	8.05	27	1.7	9.13
25	2.0	10.74	29	2.0	10.74

Although the discordant end-points would preclude the use of this method for analytical purposes, a number of important facts are brought out:

1. The alkali cannot be added to the glucose before the copper sulphate, as the alkali decomposes glucose into products which have less reducing power. Evidence of some reaction could be seen when heating the alkaline glucose solution, as it turned brown. This is not new.[1]

2. The filtrate contains something which has a slow reducing action on permanganate, and which is probably glucose oxidation products. This conclusion led to the following experiments:

a. Two solutions of glucose (five cc. of the standard) were heated in the water bath for thirty minutes. Five cc. of the acidified iron alum solution were then added, and the solution titrated with standard permanganate. One tenth cc. of the permanganate gave a definite and persisting end-point.

b. Two solutions containing five cc. of glucose (10 mg.) and two cc. of the 2 N alkali were heated in the same way, for the same length of time, and then titrated in the same manner. Here the end-point faded quickly. This proved that the iron salts were accelerating the oxidation of the glucose decomposition products by permanganate much as they had affected the tartrates.

3. The copper numbers for the various determinations in Table VI and VII are not concordant. The average value of these copper numbers however, shows some agreement. If the accelerating effect of the iron salts could be taken advantage of, or avoided, concordant analytical data might still be

[1] Hawk: "Physiological Chemistry," 227 (1923).

secured. To take advantage of the iron salts would be to employ them as catalytic agents. Thus complete oxidation of the glucose or glucose degradation products might be secured. Titrating the solution at a higher temperature should aid this further oxidation to occur.

Accordingly, 10 mg. of glucose were oxidized by an alkaline copper oxide solution as before, and then transferred to a half liter beaker. Three hundred cc. of boiling distilled water were added, and the titration completed before the temperature reached 70°C. The data are shown in Table VIII. The data show a higher copper number, but the end-point was almost impossible to determine, as will be seen by an inspection of the amount of permanganate used.

TABLE VIII

10 cc. H_2O, 5 cc. glucose (0.01 gm.), 1 cc. $CuSO_4.5H_2O$. Heat in water bath for five minutes, add 1 cc. 2M NaOH and heat 20 minutes. Titrate hot, using ferric alum, and 200 cc. boiling water.

Time of heating	Temp. of heating	cc. $KMnO_4$ used	mg. copper
23	99	9.0 −9.35	22.11
27	99	8.85−9.35	22.11
31	99	8.95−9.45	22.30
35	99	7.9 −8.3	19.63

The higher of the two values does not indicate a definite end-point, but does indicate the place where pink first persisted for probably a second or two. This method did not give complete oxidation.

Phospho-molybdic Reagent as an Oxidant for Cuprous Oxide.

The use of phospho-molybdic reagent as an oxidant for ferrous or cuprous ions was first published by Fontès and Thiovollé.[1] The clear solution is reduced by "ous" salts to give a blue color which they ascribed as probably due to lower oxides of molybdenum. When this solution is titrated with permanganate, the blue gradually disappears and goes colorless. This is the end-point, although Brode[2] recommended titrating to a pink end-point.

To determine the actual end-point, the following experiments were carried out:

1. Two samples of ferrous ammonium sulphate (Mohr's salt) each containing 0.6256 grams were titrated with standard permanganate and each required respectively 41.85 and 41.95 cc.

2. To each of two or more samples of the ferrous ammonium sulphate of similar size, 25 cc. of the phospho-molybdic reagent were added before titrating with the permanganate. Each sample required 41.9 cc. of $KMnO_4$

[1] Bull., 33, 840-44 (1923).

[2] Brode: "Determination of the Copper Number." Report of the Committee of the Cellulose Division of the American Chemical Society, Philadelphia (1926).

when "titrated to a colorless end-point." The above titrations were made at room temperature. Titrations at 90°C. gave similar results.

From the previous work with iron salts, it is obvious that phospho-molybdic reagent cannot be used if it accelerates the oxidation of glucose degradation products. Three solutions, each containing 2 cc. 2M NaOH, 10 cc. H_2O and 5 cc. (0.01 gm.) glucose were heated for three hours in a water bath at 96.5°C. At the end of the heating, solution No. 1 received 5 cc. 2N H_2SO_4, solution No. 2 received 5 cc. phospho-molybdic reagent, while solution No. 3 received 5 cc. of the ferric alum solution. Each was then titrated with the N/25 (approx) permanganate solution. Each of the solutions reduced immediately 0.5 cc. of the permanganate, equivalent to a copper number of 1.18 (1.18 mg Cu). An additional 0.25 cc. was added to each of the solutions and the slower reduction observed. The reduction in solutions No. 1 and 2 occurred at the same rate as judged by the disappearance of color, but the reduction in the solution containing the iron alum was more rapid. In another test tube, 20 cc. of the M copper sulphate solution, five cc. of glucose solution (10 mg.) and 10 cc. of water were heated to the temperature of the water bath. Two cc. of 2 M NaOH were then added, and the heating continued for 20 minutes. At the end of the heating, the contents were cooled, transferred to a half-liter Pyrex flask and 25 cc. of the phospho-molybdic reagent added to the test tube and then poured into the beaker. Two hundred cc. of distilled water were added, and the solution titrated with permanganate. At the disappearance of the blue molybdenum color, a pink end-point appeared which was satisfactory for analytical work.

It was hoped that the phospho-molybdic reagent could be used with Fehling solution, thus eliminating the necessity of filtering. To 10 cc. of sodium-potassium-tartrate (346 grams per liter) were added 10 cc. of the acidified phosphomolybdic reagent. This solution reduced permanganate only slowly in the cold. To 10 cc. of alkaline tartrate solution (B of Fehling's) 10 cc. of the acidified phospho-molybdic reagent were added. This solution also reduced permanganate slowly.

A new solution was prepared like the latter one, and then divided into two equal parts. To one part, one cc. of M. copper sulphate was added and the other part was left unchanged. The presence of copper ions accelerated the reduction of permanganate by the tartrates. Two ten mg. samples of glucose were then oxidized with Fehling solution, cooled, phospho-molybdic reagent added, and the solution diluted to 200 cc. before titrating. The results were about 50% higher than obtained by using alkaline copper solutions. From these experiments, it was concluded that phospho-molybdic reagent could not be used with Fehling solution and filtration dispensed with. However, alkaline copper solutions in which tartrates were not present could be used. The procedure is the same as outlined on p. 1452, except that 25 cc. of phospho-molybdic reagent is substituted for the iron alum.

The Oxidation of Glucose

Glucose has been oxidized by many experimenters, and in many ways, including atmospheric oxygen,[1] methylene blue,[2] hydrogen peroxide [3] and alkaline solutions of metallic oxides, such as mercuric oxide,[4] silver oxide,[5] and copper oxide. The latter is by far the most widely used for the oxidation of glucose and other reducing sugars. Fehling worked out the conditions for this reaction and found that the ratio between glucose and copper was 1:10 in equivalents or 1 molecule reduces 5 molecules of $CuSO_4$, corresponding to two and a half atoms of oxygen. But as will be seen from the data in Tables IX and X, and from the curves in Figs. 1 and 2, the words of Bang[6] have a

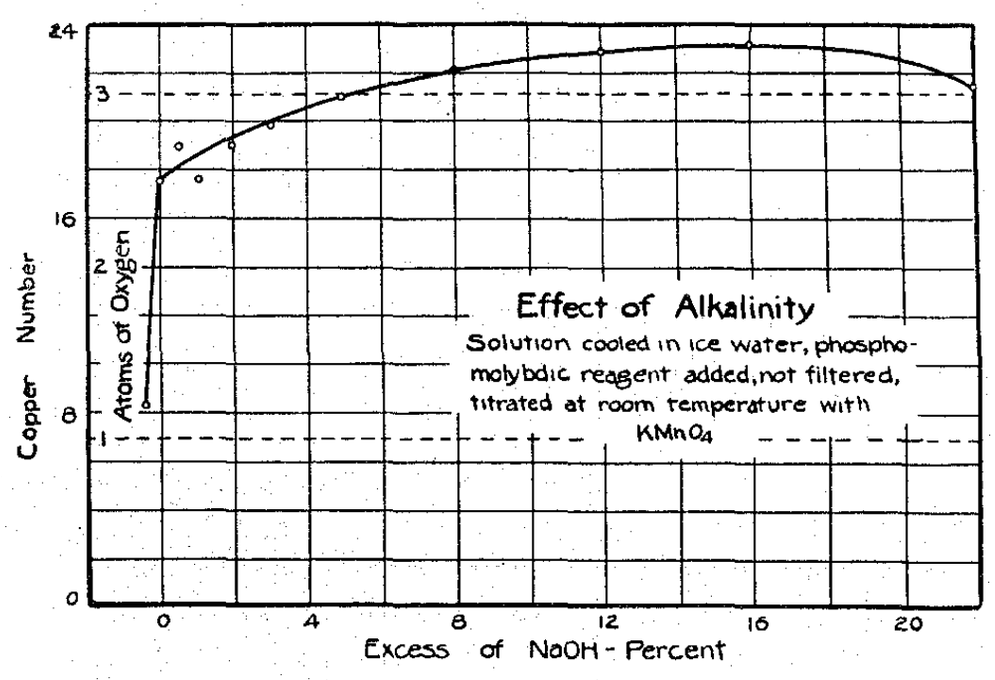


FIG. 1

significant meaning, "If one studies the analytical methods for determining reducing sugars, one will find that the simple methods are not exact and the exact methods are not simple."

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[1] Rodziszewski: Ber., **10**, 70 (1877); Traube: Ber., **7**, 115 (1874); Loew: Ber., **23**, 678 (1890); Dhar and Mittra: J. Phys. Chem., **29**, 376, 739 (1925); Spoehr: J. Am. Chem. Soc., **46**, 1494 (1924); Spoehr and Smith: **48**, 241 (1926).

[2] Knecht and Hibbert: J. Soc. Dyers and Colourists, **41**, 94-5 (1925); Ihl: Z. anal. Chem., **29**, 386 (1890); Herzfeld: Z. Vereins. deutsch. Zuckerindustrie, **13**, 234 (1886).

[3] Ber. **22**, R 125 (1889); Cross: Bevan and Smith: Chem. Centralblatt, **1898** II, 19; Spoehr: Am. Chem. J. **43**, 248 (1910); Fenton: J. Chem. Soc., **65**, 899 (1894); 75, 1 (1899; **77**, 69 (1900); Ruff: Ber., **31**, 1573 (1898); **32**, 550, 3672 (1899); **33**, 1798 (1900); **34**, 1362 (1901).

[4] Heffler: Ber., **22**, 1049 (1889); Herzfeld: Z. Vereins deutsch. Zuckerindustrie, **37**, 337 (1887); Bruhns: **36**, 110 (1886); Knapp: Ann., **154**, 252 (1870); Sachsse: J. prakt. Chem. (2) **6**, 118 (1873); Chem. Centralblatt, **1876**, 520; **1877**, 471.

[5] Kiliani: Ann., **205**, 191 (1880); Tollens: Ber., **16**, 921 (1883); Nef: Ann., **357**, 287 (1907); Erdmann: Ann., **21**, 8 (1837); Liebig: Ann., **113**, 1 (1860).

[6] Biochem. Z., **2**, 271 (1907).

The literature following Fehling's announcement was filled with exceptions and confirmations. Rigaud,[1] Stadel and Krause,[2] and Schiff[3] and Neubauer[4] confirmed the statement of Fehling that one molecule of glucose reduced 10 equivalents (5 molecules) of copper sulphate. But Boedeker,[5] Violette,[6] Vierordt,[7] Strohmer and Claus,[8] Gratma,[9] and Maercker[10] either failed to check the data of Fehling and his supporters or else had to modify the solution somewhat to check Fehling's data.

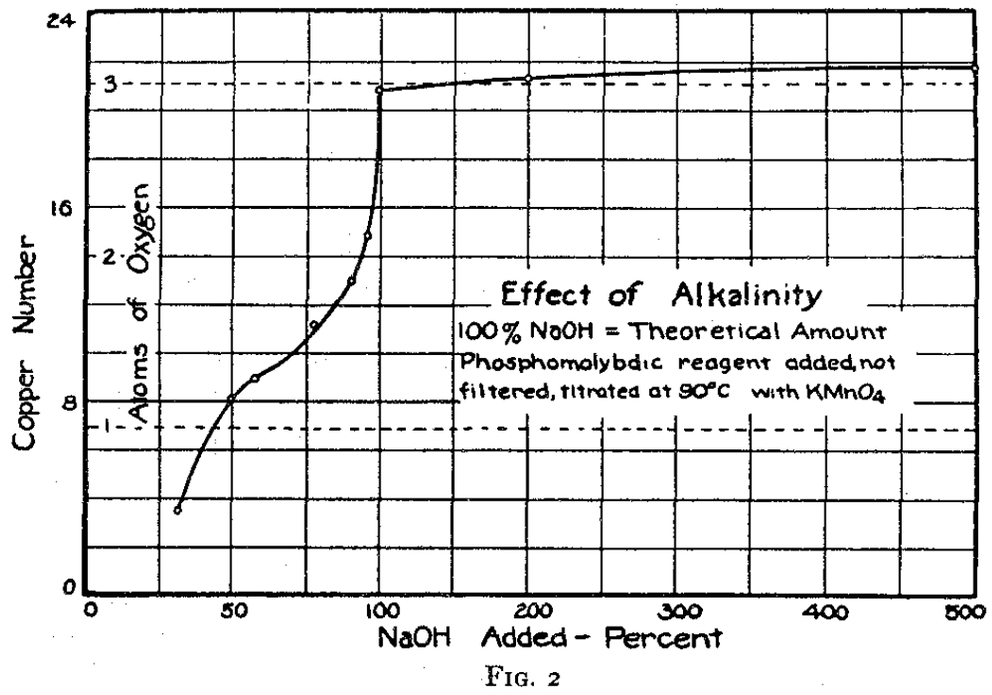


FIG. 2

In 1878 Soxhlet[11] wrote, "The estimation of many sugars by means of alkaline copper solutions and volumetric or gravimetric methods has had such an extended application for thirty years in the different branches of applied chemistry, that one has been led to believe that the method conformed to a natural law beyond any doubt. A few analyses of sugar with Fehling solution made on pure sugars has led me to an opinion so different from the customary one that I undertook exhaustive experiments to prove the facts." The next year, Soxhlet stated the facts as he saw them,[12] "One mole of glucose does not always reduce five moles of copper, the value varying from 5.5 moles to 4.85

[1] Ann., **90**, 297 (1854).
[2] Mittheil naturf. Gesellschaft in Zürch, **1854**, 473; Ann., **104**, 330 (1857).
[3] Ann., **104**, 330 (1857).
[4] Archiv. Pharmacie, (2) **71**, 278.
[5] Heule und. Pfeüffer's Zeitschrift, **6**, Heft 2.
[6] "Dosage du Sucre," (1868).
[7] Ann., **177**, 32 (1875).
[8] Chem. Centralblatt, **1877**, 699.
[9] Z. anal. Chem. **17**, 155 (1878).
[10] Chem. Centralblatt, **1878**, 584.
[11] Chem. Centralblatt, **1878**, 218.
[12] Bied. Centralblatt., **1879**, 370.

TABLE IX

Oxidation of Glucose with Alkaline Copper Solutions at 99°C.

25 cc. Phospho-molybdic reagent was added without filtering—after cooling the reaction tubes in ice to 22–25°C. The solution was then transferred to 500 cc. Pyrex beakers, diluted to 200 cc. stood for five minutes and titrated with standard permanganate.

10 mg. glucose in 5 cc. H_2O.

Time	Alkalinity of Sol.	H_2O added	M-$CuSO_4$ added	2M-NaOH added	$KMnO_4$ cc.	Mg. Cu × 2.38	Avg.
30	−½%	10	2 cc.	1 cc.	3.5	8.33	8.27
					3.45	8.21	
30	0%	10	1 cc.	1 cc.	7.55	17.97	17.67
					7.30	17.37	
30	½%	10	1 cc.	2 cc.	8.10	19.27	19.16
					8.00	19.04	
30	½%	10	1 cc.	2 cc.	7.85	18.68	18.86
					8.00	19.04	
30	1%	8	1 cc.	3 cc.	7.4	17.85	17.73
					7.4	17.61	
30	2%	6	1 cc.	0 cc.	8.0	19.04	19.04
					8.0	19.04	
30	3%	4	1 cc.	7 cc.	8.3	19.75	19.87
					8.4	19.99	
30	5%	0	1 cc.	11 cc.	8.9	21.2	21.49
					9.15	21.78	
30	8%	6 cc.	1 cc.	34%	9.6	22.85	22.37
				4cc.	9.2	21.9	
30	12%	4 cc.	1 cc.	34%	9.8	23.32	22.85
				6cc.	9.4	22.37	
30	16%	2 cc.	1 cc.	34%	9.7	23.09	23.15
				8cc.	9.75	23.20	
30	22%	0 cc.	1 cc.	34%	9.1	21.65	21.66
				11cc.	9.15	21.77	

TABLE X

Oxidation of Glucose with Alkaline Copper Solutions at 99°C.

25 cc. Phospho-molybdic reagent was added without filtering or cooling, the contents transferred to a 500 cc. Pyrex beaker, 300 cc. boiling water added, the whole heated to 90°95°C. and titrated with standard permanganate.

Time	Per cent* Alkali	H_2O added	M-$CuSO_4$ added	2M Alkali	cc. $KMnO_4$	Mg. Cu × 2.3657	Avg.
30	33⅓%	10	3 cc.	1 cc.	1.50	3.55	3.73
					1.65	3.90	
30	33⅓%	10	3 cc.	1 cc.	1.50	3.55	3.43
					1.40	3.31	
30	50%	10	2 cc.	1 cc.	3.40	8.04	8.10
					3.45	8.16	
30	66⅔%	10	1.5 cc.	1 cc.	3.75	8.87	8.87
					3.75	8.87	
30	80%	10	1.25 cc.	1 cc.	4.70	11.11	11.29
					4.85	11.47	
30	90%	10	1.11 cc.	1 cc.	5.5	13.01	12.78
					5.3	12.54	
30	95%	10	1.05 cc.	1 cc.	6.45	15.25	14.78
					6.25	14.78	
30	95%	10	1.05 cc.	1 cc.	6.05	14.31	
					6.25	14.78	
30	100%	10	1.00 cc.	1 cc.	8.8	20.82	20.87
					8.85	20.93	
30	200%	10	1.00 cc.	2 cc.	8.9	21.05	21.29
					9.2	21.76	
30	200%	10	1.00 cc.	2 cc.	9.0	21.29	
					8.9	21.05	
30	500%	6	1.00 cc.	5 cc.	9.25	21.88	21.59
					9.00	21.29	

*100% alkali is the amount required to convert all of the $CuSO_4$ to $Cu(OH)_2$.

moles, and varies with the dilution, and amount of Fehling solution in excess. The solutions keep better if not mixed. Since the amount of glucose is unknown, the method is not good for analyses, as the proportional changes affect it." Finally[1] Soxhlet said that, since the method of estimating reducing sugars depended upon the excess of Fehling solution, and if one did not know how much sugar was present, he could not regulate this excess, "it was clear that an analytical estimation by means of alkaline copper solutions was impossible."

Tollens and Rodewald[2] although cognizant of the work of Soxhlet, reached the same conclusions more or less independently.

The work of Soxhlet had a stimulating effect on analytical sugar methods. Many felt as Scheibler[3] who said, "I have given the copper number my attention, partly by working at it, partly by letting qualified students work at it in the laboratory. Some of the results we got were inexplicable. However, after the paper of Soxhlet, it was as clear as if the scales had fallen from my eyes. I had obtained the same results (as Soxhlet) but had not had the courage to express them in the clear form as has happened here." The most of the investigators, however, felt as Allihn,[4] who, when he saw Soxhlet's conclusions, proceeded to work out a new method which substituted 250 grams of potassium hydroxide per liter of alkaline tartrate solution in place of the sodium hydroxide, the composition of the copper salt and the tartrates remaining unchanged.

Since 1880, very few people have studied this reaction in order to determine its further limitations, but there is one other piece of work which deserves some consideration, the work of Kjeldahl.[5] He found that the copper number decreases as surface exposed to air is increased, due to surface oxidation. Brown, Morris and Millar[6] found that Kjeldahl's results were about 6 per cent higher than theirs where no precautions were taken to exclude air. Quisumbing and Thomas[7] found that a layer of toluene or a cover-glass was equally effective in preventing surface oxidation. The following data in Table XI confirm the fact that a vessel open to the atmosphere causes a lower copper number to be obtained.

Kjeldahl also found that diluting a solution caused a lower copper number to be obtained. Since the reaction mixture is homogeneous, the variables which define homogeneous reactions will exert their influence here. Any change in the concentration, then, will give a change in the copper numbers. Quisumbing and Thomas[8] have shown that the proper concentration of alkali

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[1] J. prakt. Chem., (2) **21**, 227-317 (1880).
[2] Ber., **11**, 2076 (1878).
[3] Z. Vereins Rübenzuckerindustrie, **1878**, Juniheft.
[4] J. prakt. Chem., (2) **22**, 46-96 (1880).
[5] Z. anal. Chem., **35**, 344-68 (1896).
[6] J. Chem. Soc., **71**, 94 (1897).
[7] J. Am. Chem. Soc., **43**, 1503-26 (1921).
[8] J. Am. Chem. Soc., **43**, 1503-26 (1921).

to use is that which gives nearly a maximum copper number. If such a solution is diluted, the subsequent alkali concentration will be less and so the copper number will fall off.

Kjeldahl also found that the amount of spontaneous reduction of the Fehling solution was proportional to the time of heating. This fact will cause no error in methods that employ volumetric analyses for determining the copper number, and may not prevent obtaining concordant results by gravimetric methods.

TABLE XI

Table showing Effect of Surface Oxidation

Oxidation of 20 mg. Glucose with Alkaline Copper Solutions

Phospho-molybdic reagent was added without filtering and titrated with permanganate at 90°C. in 200 cc. H_2O. Pyrex test tubes $\frac{3}{8}'' \times 6''$ open to the air were used.

5 cc. H_2O, 20 mg. glucose in 10 cc. H_2O; 1 cc. $CuSO_4$; Heat—Add 1 cc. NaOH.

Time	Temp.	Remarks	cc. $KMnO_4$	Cu. in mg. $\times 2.3657$*
20	99	50 cc. Phospho-	14.5	34.30
30	99	molybdic reagent	14.6	34.54
50	99	used	14.0	33.12

*1 cc. $KMnO_4$ 2.3657 mg. Cu.

Pyrex test tube $1'' \times 8''$ with cover glasses used. 5 cc. H_2O, 20 mg. glucose in 10 cc. H_2O; 1 cc. $CuSO_4$; Heat—Add 1 cc. NaOH.

Time	Temp.	Remarks	cc. $KMnO_4$	mgCu $\times$ 2.3657
20	99	Watch or cover	16.9	39.98
25	99	glass used with	16.7	39.50
30	99	nitrogen gas	16.5	39.03

He found further that the amount of spontaneous reduction depended upon the alkalinity of the solution, and increased if any definite concentration was diluted. These results have been confirmed by Jovitschitsch,[1] Rosenthaler,[2] Watts-Tempany[3] and others[4] who found that Fehling solution precipitated CuO unless the alkalinity was high.

If the concentration of the glucose is doubled, none of the methods will give twice the copper number throughout their entire range. This can be seen by an inspection of the data in Table XII.

Lottermoser[5] found in studying two solutions of $AgNO_3$ and KBr, that if they were mixed in exactly equal amounts, the AgBr precipitated and the supernatant liquid remained clear. If an excess of either KBr, or $AgNO_3$

[1] Ber., **30**, 2431 (1897).

[2] Archiv Pharmacie, **241**, 589 (1903).

[3] Chem. Centralblatt, 1908, I, 1576.

[4] Gerock: Ber., 30, 2865; Siegfield; 3133 (1897); Rosenhein, Schidrowitz: Chem. Centralblatt, **1898**, I, 417, 798.

[5] J. prakt. Chem., (2) **72**, 39 (1905).

was added, however, the solution became turbid, due to the adsorption of one of the ions present in excess, and a resultant peptization. When the alkali present is considerably less than the amount needed to precipitate all the copper sulphate as cupric hydroxide, the precipitate is granular. As the al-

TABLE XII

Showing effect of doubling glucose, alkaline copper solution remaining constant.

Pyrex test tubes 1″ × 8″, filled with nitrogen and closed with a cover glass.

10 cc. H_2O, 5 cc. glucose (10 mg.) 1 cc. $CuSO_4$. Heat. Add 1 cc. NaOH.

Time	Temp.	cc. $KMnO_4$	mg. Cu. × 2.3657
20	99	8.90	21.05
30	99	8.95	21.17

5 cc. H_2O, 10 cc. glucose (20 mg.) 1 cc. $CuSO_4$. Heat. Add 1 cc. NaOH.

Time	Temp.	cc $KMnO_4$	mg. Cu. × 2.3657	Theoretical
20	99	16.95	40.10	42.10
20	99	16.75	39.62	
30	99	16.55	39.15	42.40
30	99	16.75	39.62	

*For a further confirmation of the data in this table, see Tables XIV, XV, and XVI, and Figs. 3 and 4.

kalinity approaches 100 per cent, the peptization increases. Likewise, on the alkaline side of the 100 per cent mark, the peptization is strong, so strong that the solution cannot be filtered. As the alkalinity increases, the flocculation increases, and finally a concentration is reached where the precipitate settles out and is easily filtered. This is the concentration which most experimenters have recommended for their method, since a good precipitate of cuprous oxide is necessary for any filtration process, in order to prevent mechanical loss. No investigation was made concerning the iso-electric point of this system. It should be remarked, however, that the colloidal nature of the copper oxide is a valuable aid in its use as an oxidant.

Although it was mentioned on p. 1449 that the removal of the ferric ions from solution to form a complex iron salt stopped the accelerated reduction of permanganate by tartrates in acid solution, this fact was not used until after most of the data in this paper had been obtained. It did suggest, however, that perhaps iron alum could be used to oxidize the cuprous oxide, the remaining unused ferric ions be removed through the formation of the complex and the induced reaction be prevented. Two substances have been found which will accomplish this result, sodium fluoride and sodium pyrophosphate. (It is not to be inferred that other alkali fluorides or pyrophosphates could not be used.)

1. Sodium Fluoride. Five cc. of the acidified ferric alum solution (containg 1.25 grams H_2SO_4 and 0.5 gm. ferric alum, which is equivalent to 8 atoms of oxygen) and 2 grams of sodium fluoride[1] were dissolved in 100 cc. of water. The additon of a few drops of potassium ferrocyanide gave no color of Prussian blue, indicating that all the ferric ions had been removed. If the acidity of the solution was increased to $2.5-3\%$ the complex decomposed and the familiar blue test for ferric ions appeared.

Using 2 gm. sodium fluoride with 5 cc. of acidified iron alum, the results given in Table XIII were obtained. These experiments were carried out in a

TABLE XIII

Oxidation of Cuprous Oxide*

0 cc. H_2O; 1 cc. $CuSO_4$.5 cc. glucose (10 mg.). Heat. Add 11 cc. 2N.NaOH. Time 30 min.

Remarks	Temp.	cc. $KMnO_4$	mg. Cu.
Phospho-molybdic Reagent	99	9.0	21.29
	99	9.2	21.9
Ferric alum—excess	99	10.9	25.98
Fe$^{\cdot\cdot\cdot}$ ions not removed	99	10.5	24.99
Ferric alum—excess	99	9.3	22.13
Fe$^{\cdot\cdot\cdot}$ ions removed by adding 2.0 gms. NaF diluting to 200 cc. and titrating cold.	99	9.45	22.49
	99	9.25	22.00
	99	9.60	— —
Use 5 cc. Fe alum and 10 cc. saturated solution of sodium pyrophosphate at room temperature	98.5	9.30	22.13
	98.5	9.55	22.72
	98.5	9.40	22.37

*A 500 cc. Bakelite beaker was used in these experiments.

500 cc. Bakelite beaker furnished by the Bakelite Corporation. Great appreciation is due this company for their kind cooperation.

Although the results obtained by using ferric alum and NaF were slightly higher than with the phospho-molybdic reagent, the large decrease over the results obtained by having the ferric ions in excess, indicated that ferric ions were responsible for the induced reaction. Furthermore, tartrates heated with acidified iron alum on a water bath for thirty minutes gave a test for ferrous ions with potassium ferricyanide, although this test did not indicate the presence of many ferrous ions. Heating tartrates with acidified iron alum on a water bath for several hours did not give a heavier test for ferrous ions, indicating that the oxidation of tartrates by ferric salts in acid solution did not proceed far.

Having met with marked success in reducing the catalytic effect of ferric ions in alkaline copper oxide solutions, it was hoped that the same method might be employed with Fehling solution. Accordingly, glucose was oxidized

[1] Two grams of sodium fluoride were required to remove all the ferric ions in 5 cc. of ferric alum, from solution.

with Fehling solution, neutralized, acidified iron alum and NaF added, and then titrated with standard permanganate. The tartrates reduce permanganate fairly rapidly in the cold, this reaction being accelerated by copper ions as already indicated on p. 1457, and this method cannot be used for quantitative work. This is shown by the following experiments:

Ten mg. of glucose were estimated under the conditions given on p. 1465, except that Rochelle salts were added. (Enough of "B" of Fehling's solution was added to give the 0.88 gms. of NaOH contained in 11 cc. of the 2N NaOH which had been used. This was 9 cc.) All other conditions were kept the same. These solutions required about 50% more $KMnO_4$ to give the first trace of an end-point which quickly disappeared, due to the reducing power of the tartrates.

Doubling the copper concentration and keeping all other conditions constant had no noticeable effect on the end-point. Increasing the copper concentration 1100%, keeping the acidity of the solution the same as before, caused the end-point to be about 6% higher, although the results were concordant. This was probably due to the deeper blue of the titration solution obscuring the end-point and the excess was needed to give a pink color which deepened the blue copper color, the end-point which was used.

The effect of sodium fluoride on the reducing power of ferrous salts is interesting. To a solution of copper sulphate some ferrous ammonium sulphate and sodium fluoride were added in the order named. The ferrous salt had no effect until the sodium fluoride was added, and then cuprous oxide was precipitated. This reaction occurs because the reduction potential depends on the ratio between ferrous and ferric ions. Adding sodium fluoride to the solution removes the ferric ions and consequently increases the reduction potential of ferrous ions to such a point that they can reduce copper sulphate. The increase in the reduction potential of a mixture of ferrous and ferric sulphates upon the addition of fluoride ions has previously been cited by Peters.[1]

2. Sodium pyrophosphate. The second substance which can be used to form a complex with ferric ions and thus remove them from solution is sodium pyrophosphate. This salt does not form complex with ferrous ions though the usual tests for these ions do not indicate their presence. The ferric pyrophosphate is easily decomposed by acids so that it is necessary to use solutions containing not over 0.1% H_2SO_4 by weight. This ferrous solution is easily oxidized by atmospheric oxygen, and unnecessary stirring must be eliminated. The results of the analyses of glucose by alkaline copper oxide using iron alum to oxidize the cuprous oxide and sodium pyrophosphate to remove the unused ferric ions from solution, is given in Table XIII.

The pyrophosphates have been studied by Job,[2] Pascal,[3] Rosenheim[4] and his school, and Spoehr.[5]

[1] Z. physik. Chem., **26**, 193 (1898).
[2] Job: Ann. Chim. Phys., (7), **20**, 208 (1900).
[3] Pascal: Ann. Chim. Phys., (8) **16**, 359, 522 (1909).
[4] Ber., **48**, I, 582 (1915); Z. anorg. allg. Chem., **153**, 126 (1926).
[5] Spoehr: J. Am. Chem. Soc., **46**, 1494 (1924); Spoehr and Smith: J. Am. Chem. Soc., **48**, 107, 236 (1926).

Other Quantitative Methods of estimating Glucose

Mention has previously been made (p. 5200) that following the work of Soxhlet, investigators contented themselves with the preparation of various empirical methods, and tables based on these methods, for the estimation of sugars. Probably fifty, or more[1] different tables and methods have been used for the determination of glucose and other reducing sugars, in industries,[2] laboratories and hospitals.[3]

These methods tend to fall into three general groups as regards the operations:

1. The use of NaOH as alkali.
2. The use of KOH as alkali.
3. The use of carbonates as alkali.

In Tables XIV, XV, and XVI are given data from Munsen and Walker's[4] tables, Allihn's[5] and Soldiani[6] respectively.

These data were obtained as follows: The copper number for 10 mg. of glucose was taken as a standard, and the copper number for 10 mg. of glucose at that concentration, calculated. These calculated copper numbers were then plotted as ordinates and the total weight of glucose in the solution (milligrams) plotted as abscissae. Since the volume of the Fehling, Allihn or Soldiani solution is constant, the two variables are the glucose concentration and the copper number.

We see from an inspection of the data from Munsen and Walker's Table that the most dilute solution gives the highest copper number, and as the concentration of glucose increases, the copper number falls off. This was confirmed by Maercker,[7] Ulbricht[8] and Soxhlet[9] and more recently by Quismbing and Thomas[10] and Bertrand.[11] Allihn's method gives a maximum in the

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[1] For a list of these tables see Browne: "Handbook of Sugar Analysis" (1912); Hawk: "Physiological Chemistry."

[2] Märcker: Centralblatt, **1878**, 584; Soxhlet: loc. cit.; Fehling: loc. cit.; Meissl: Z. Verein deutsch. Zuckerindustrie, **29**, 1050 (1879); Herzfeld: **35**, 985 (1885). Kjeldahl: Z. anal. Chem., **35**, 344-68 (1896).

[3] Soldiani: Gazz., **6**, 322 (1876); Soldiani, Ost: Ber., (23) 1025 (1890); Bang: Biochem. Z., **2**, 271 (1907); Hönig and Jesser: Monatshefte, **9**, 562 (1888); Brown, Morris and Millar: J. Chem. Soc., **71**, 96, 281 (1897); Bertrand: Bull., **35**, 1285 (1906); Defren: J. Am. Chem. Soc., **18**, 749 (1895); Munsen and Walker: **28**, 663 (1895); **29**, 541 (1896); **34**, 202 (1901); Kendall: **34**, 317-41 (1912); Barfoed: Z. anal. Chem., **12**, 27 (1873); Allein and Gaud: J. Phar. Chim., (3), **30**, 305-7; Koch and Rushan: J. Soc. Chem. Ind., **13**, 1227 (1894); O'Sullivan: J. Chem. Soc., **30**, 130 (1876); Sachsse: J. prakt. Chem., 118 (1873); Knapp: Ann., **154**, 252. Lowe: Z. Anal. Chem., **9**, 20 (1870); Shaffer: J. Biol. Chem., **19**, 228 (1914); Peters: J. Am. Chem. Soc., **34**, (11) 928 (1912); Kendall: **34**, 317-41 (1912); Folin: J. Biol. Chem., **67**, 357 (1926); Folin and Wu: **33**, 513 (1918); Benedict: J. Biol. Chem., **3**, 101-7 (1907); **64**, 207 (1925); Quisumbing and Thomas: J. Am. Chem. Soc., **43**, 1503 (1921); Pick: Chem. Abs., **19**, 3028 (1925); Peguerier: Chem. Abs., **19**, 3441 (1925).

[4] Allen: "Commercial Organic Analysis," **1**, 401.

[5] Wiley: Agricultural Analysis," 156 (1897).

[6] Wiley: Agricultural Analysis," 260, (1897).

[7] Chem. Centralblatt, **1878**, 584.

[8] Chem. Centralblatt, **1878**, 392.

[9] loc. cit.

[10] J. Am. Chem. Soc., **43**, 1503-26 (1921).

[11] Bull., **35**, 1285 (1906).

curve. This has been verified by Peters[1] and Shaffer.[2] Glendinning[3] noted that KOH and NaOH had different effects on maltose but claimed that dextrose and invert sugar gave the same results with either alkali. Pflüger[4] and Kendall[5] used KOH and carbonates respectively, but neither obtained a maximum in the curve. Pflüger used Allihn's method while Kendall worked out a new one employing salicylic acid with the carbonates. Sodium salicylate would not serve in this method.

Since the Allihn and Munsen and Walker methods are the ones which have been adopted by A.O.A.C.[6] there is little likelihood of serious errors in the data. However, unless the effect of the alkali is specific, it seems that the general direction of the curves should be the same. The cause for this is at present unknown. The data are given in Tables XIV, XV, and XVI and represented graphically in Fig. 3.

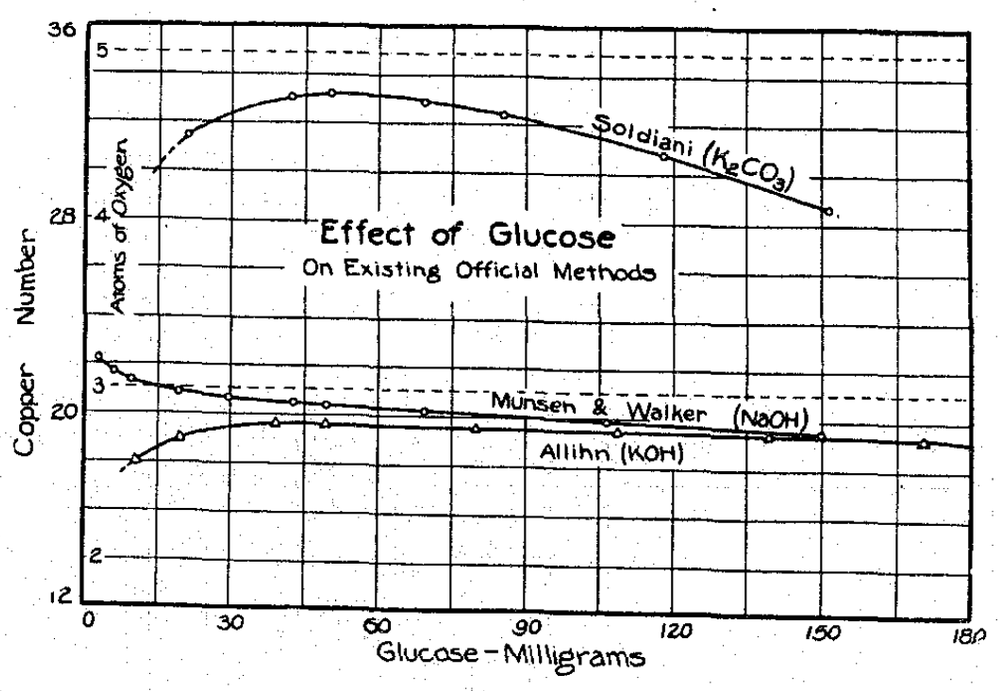


FIG. 3

The copper number of Soldiani's[7] solution for 10 mg. of glucose is about 50 per cent higher than with sodium hydroxide. This result was unexpected since a very dilute solution of alkali gave no indication of such a high copper

[1] Peters: J. Am. Chem. Soc., **34**, 928 (1912).

[2] Shaffer: J. Biol. Chem., **19**, 288 (1914)

[3] Glendinning: J. Chem. Soc., **67**, 999 (1895).

[4] Pflüger's Archiv, **69**, 399.

[5] J. Am. Chem. Soc., **34**, 367, (12).

[6] Reference A. O. A. C., 2nd. Ed., p. 190, 196 (1925).

[7] It is not possible here to discuss the merits and demerits of Soldiani's solution. The following references, however, will present a cross-section of technical opinion concerinig its use: Schiff: Ber., **9**, 1126 (1876). Soldiani: Gazz., **7**, 332 (1886); Vodenbender and Schiller: Z. Vereins deutschen Rübenzuckerindustrie, **1887**, 145; **1888-1890**; Soldiani: **1888**, 722 **1889**, 933; **1890**, 19, 51; Ost: Ber., **23**, 1035; Chem. Ztg., **19**, 1784, 1829 (1890); Bang: Biochem. Ztg., **2**, 27 (1907); Benedict: J. Biol. Chem., **3**, 101 (1907); Parcus: Chem. Ztg. **12**, 1316 (1889); Holleman-Walker: "Textbook of Organic Chemistry," 212 (1924).

number, as will be seen from Fig. 1. The higher results obtained by using carbonates were checked. Ten mg. of glucose were oxidized by copper oxide in carbonate solutions as indicated in Table XVII, and Fig. 4.

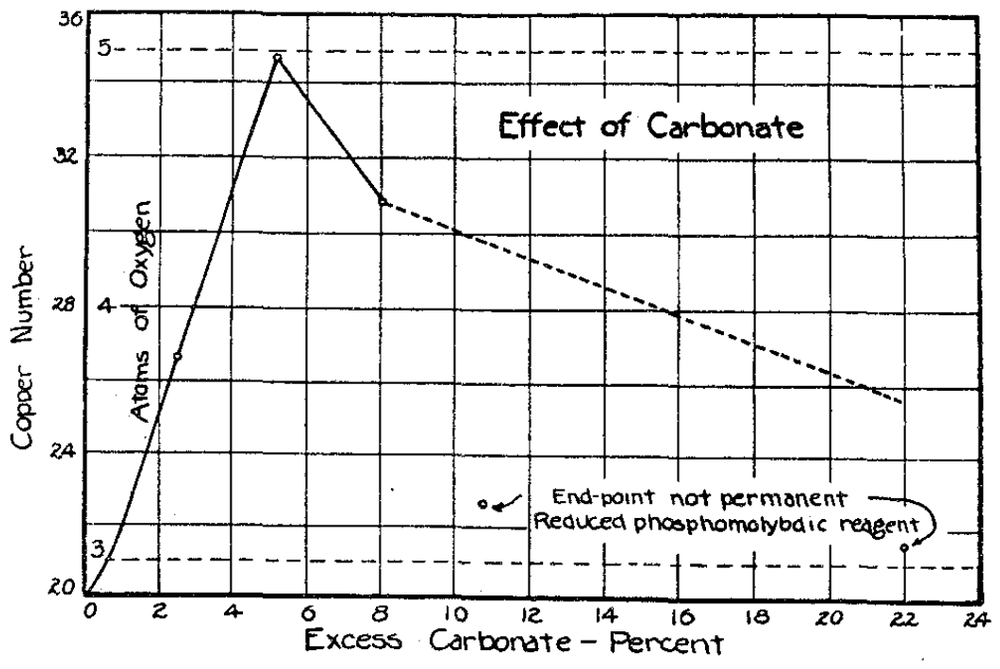


FIG. 4

TABLE XIV

Change in Copper Number for Glucose as Concentration increases. NaOH as Alkali—Munsen and Walker Method.

Glucose Mg. present	Copper Number (Mg)	Copper Number Calc. for 10 mg. glucose	Total Decrease per cent
4.0	8.9	22.25	
7.0	15.1	21.57	
10.0	21.3	21.30	
20.0	41.7	20.85	
30.0	62.2	20.73	
42.0	86.2	20.52	17
50.0	102.0	20.40	
70.0	141.2	20.17	
107.0	211.0	19.72	
150.2	289.6	19.28	
200.1	374.8	18.73	
237.4	435.3	18.33	

The maximum copper number is approximately 35, equivalent to five atoms of oxygen, which is much higher than the results given in Tables XV or XVI, where free alkali is used. The theory for this is considered on pp. 1472-6. These results were obtained by adding the copper sulphate to the glucose, heating, and then adding the carbonate. The carbonate can be added to the glucose,

TABLE XV

Change in Copper Number for Glucose as Concentration increases.
KOH as Alkali—Allihn Method

Glucose Mg.	Copper Number	Copper Number Calc. for 10 mg.	Total Decrease
9.0	16	17.77	
10.0	18	18.0	
20.4	39	19.12	Increase
40.3	79	19.6	
50.4	99	19.64	Maximum
80.1	151	19.60	
110.0	214	19.45	
140.0	270	19.30	Decrease
172.0	328	19.30	
190.0	360	18.95	
249.0	463	18.60	

TABLE XVI

Change in Copper Number for Glucose as Concentration increases.
Na_2CO_3 as Alkali Soldiani Method
K_2CO_3

Glucose present mg.	Copper Number	Copper Number Calc. for 10 mg. G.	
21.8	70.	31.4	
41.0	135	32.9	Increase
50.0	165	33.0	
70.1	230	32.8	Maximum
85.0	275	32.3	
119.0	365	30.7	Decrease
152.3	435	28.6	

before the copper sulphate, if the heating is quickly done. Longer heating causes the glucose to decompose. This is evidenced by a brown coloration of the solution and by a lower copper number, 10 milligrams of glucose giving, after 80 minutes, a copper number of 4.3 (Compare with page 1455).

Benedict,[1] Ost[2] and Kendall[3] each got higher copper numbers when carbonates were used, than by using free alkali.

[1] J. Biol. Chem., **3**, 101-7 (1907).
[2] Ost: Ber., **23**, I, 1035 (1890).
[3] J. Am. Chem. Soc., **34**, 317-41 (1912).

TABLE XVII

Copper Number of Glucose obtained by Soldiani-Ost Solution[1] Volumetric Analysis using Phosphomolybdic Reagent. Temp. 99°C. Volume of Solution 31 cc.

Time	H_2O added	$CuSO_4$ added	Glucose added	K_2CO_3[2] $KHCO_3$	cc. $KMnO_4$	mg. Cu × 2.38	Per cent Excess CO_3 (Approx.)
30	20	1 cc.	10 mg. in 5 cc.	5 cc.	11.3	26.89	2.5%
						26.54	
	20	1 "	"	5 cc.	11.0	26.18	
30	15	1 "	"	10 cc.	14.8	35.22	
						34.63	5.22%
	15	1 "	"	10 cc.	14.3	34.03	
30	10	1 "	"	15 cc.	13.1	31.17	
						30.82	8.1%
30	10	1 "	"	15 cc.	12.8	30.46	
	5	1 "	"	20 cc.	9.7	23.08	
						22.61	10.84%
	5	1 "	"	20 cc.	9.3	22.13	
	0	1 "	"	25 cc.	9.3	22.13	16.05%
	0	1 "	"	25 cc.	8.9	21.18	

[1] Soldiani-Ost: Ber., 23 I, 1035 (1890).
A—23.5 gms. $CuSO_4$ in 500 cc.
B—250 gms. K_2CO_3 in 500 cc. } 1000 cc.
100 " $KHCO_3$

[2] K_2CO_3 – $KHCO_3$ made as B. above.

Mechanism of the Oxidation

It will be remembered that in the introduction it was stated that a copper number of 7.068 was equivalent to one atom of oxygen per molecule of glucose being used. None of the data or the curves, that have been presented, indicate an abrupt change in copper number values showing a change in consumption from one to two atoms, from two to three, etc. Instead, the curves are generally smooth and may indicate a fraction of an atom of oxygen. The only answer to this is that we are dealing, not with one reaction, but a number of them. Consequently, the amount of copper oxide reduced may be equivalent to a *fraction* of a molecule.

What are these reactions? Browne[1] says, "The simple sugars and certain of the disaccharides, as maltose and lactose, have the property of reducing alkaline solutions of many metallic salts, such as those of copper, silver, mercury and bismuth. This reaction, which is common to most aldehydes, is due to the withdrawal of oxygen from the metallic base, the latter being pre-

[1] "Handbook of Sugar Analysis," pp. 334-5, (1912).

cipitated either as a suboxide or in the metallic form. The aldehyde group of the sugar molecule is oxidized by the oxygen withdrawn from the metallic base to the acid carboxyl group as indicated in the following general equation:

$$RCHO + {}_2CuO = RCO_2H + Cu_2O$$

"The above, however, marks only the beginning of the reaction, for upon heating, the oxidation of the sugar molecule usually proceeds with the conversion of alcohol (secondary) into carboxyl group."

Lowy and Harrow[1] indicate the same reaction as Browne, while Bernthsen and Sudborough[2] say that reducing sugars show the properties characteristic of aldehydes and ketones.

Glucose is an aldehyde sugar and its first oxidation product is gluconic acid. This product then should be formed from the first reaction according to Browne, and this oxidation should give a copper number of 7.068 for 10 mg. of glucose.

Kiliani[3] heated sodium or potassium gluconates, saccharates, lactates and mucates (mucic acid) with Fehling solution and found that none of them had any reducing effect. Sohst and Tollens[4] saw this statement of Kiliani's and proceeded to verify it. Herzfeld[5] synthesized gluconic acid and found that it does not reduce Fehling solution. In view of these contradictory statements, samples of calcium gluconate (Eastman 1091) and gluconic acid[6] were heated with Fehling solution and no reduction noted. If the statement of Browne and of Lowy and Harrow is correct, then the maximum copper number for 10 mg. of glucose would be 7.068, since it would oxidize to gluconic acid which cannot further reduce Fehling solution. Consequently we must conclude that the oxidation of the carbonyl group to the carboxyl is not the primary step in the oxidation of glucose.

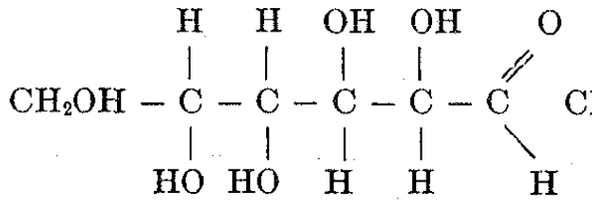
However, we have seen from curves I, II, III and IV that oxygen in amounts up to five atoms per molecule of glucose are used. What is the nature of the reaction?

Effect of Alkali on Glucose

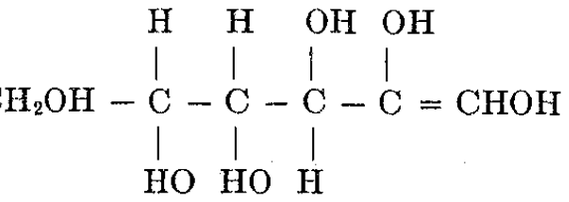
A number of years ago, Lobry de Bruyn and Alberda van Ekenstein[7] postulated that in alkaline solutions, the hexoses tended to form an equilibrated mixture as follows: d-glucose $\rightleftarrows$ d-mannose $\rightleftarrows$ d-fructose $\rightleftarrows$ d-pseudo fructose. In a subsequent paper, Nef[8] stated that, in addition to the above four, two others must be present, d-allose and d-lactose. Proceeding along stereo-chemical lines, Nef concluded that after equilibrium had been attained in alkaline solutions, glucose would have been converted into an equilibrated mixture containing 116 possible substances. To account for this equilibrium

[1] "Introduction to Organic Chemistry," 165 (1924).
[2] "Textbook of Organic Chemistry," 321 (1925).
[3] Ber., **14**, 2529 (1881).
[4] Ann., **245**, 8 (1888).
[5] J. Chem. Soc., **46**, 423 (1884).
[6] Prepared by Mr. Beach of the Organic Dept.
[7] Rec. Trav. chim., **14**, 158, 203 (1895); **15**, 92 (1896); **16**, 257 (1897); 19, 1 (1900).
[8] Ann., **357**, 254 (1907).

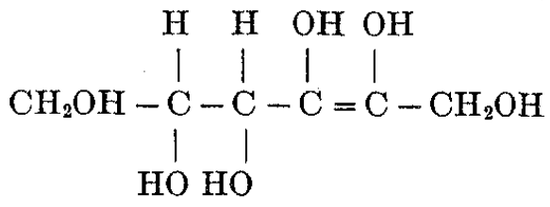
Nef proposed the theory of enediol formation "as a development of the Wohl-Neuberg[1] enediol conception of sugar structures." According to this theory, glucose in alkaline solution undergoes the following degradation:



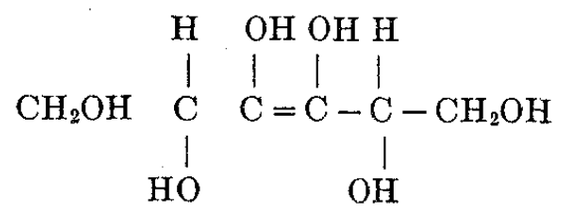
d–glucose



d–glucose 1,2 enediol



d–glucose, 2,3, enediol



d–glucose, 3,4, enediol

and then the molecule proceeds to split at the double bond, giving rise to many degradation products. In support of his theory, Nef oxidized 114 grams of glucose with 382.5 grams of hydrated copper sulphate and 183.9 grams of sodium hydroxide. This solution gives about 12 grams of oxygen and contained about 50% excess alkali.

From this he obtained:

3.83	grams	CO_2
14.71	"	formic acid
22	"	glycollic acid
14	"	glyceric acid
30	"	tri-oxy-butyric acid
30	"	hexonic acid
114.54	TOTAL	

When oxidizing agents are not present, there is a conversion into lactic, acetic, and formic acids; but hydroxy acids, acetol, and pyruvic acid are not obtained.[3] If the sugar molecule is sensitive to alkali and undergoes enolization and subsequent fission, the type of product which is formed should be dependent upon the concentration of the alkali. In the equilibrium 1,2 enediol $\rightleftarrows$ 2,3 enediol $\rightleftarrows$ 3, 4 enediol, the absolute quantities of each of these constituents should be a function of the alkalinity. The process of enolization required the removal of the hydrogen from one carbon by an active group, such as the aldehyde, or ketone group. The hydrogen which is most easily extracted should be the one first adjacent to the active C group, and in the least alkaline solutions, this type of enolization should predominate. This

[1] Hudson: "A Survey of American Chemistry," **1**, 185 (1927).
[2] Evans and others: J. Am. Chem Soc., **48**, 2667 (1926).

would seem to happen, as Upson and Power[1] found that about 20% of the total acid formed by the oxidation of glucose in saturated calcium hydroxide solutions was formic, which could result from 1,2 fission. Furthermore, Jensen and Upson,[2] found that if carbonate solutions were used, (Soldiani's reagent) 30.86 grams of formic acid were formed as compared to 31.6 grams for all other acids estimated. They did not estimate all the acidic material present, however.

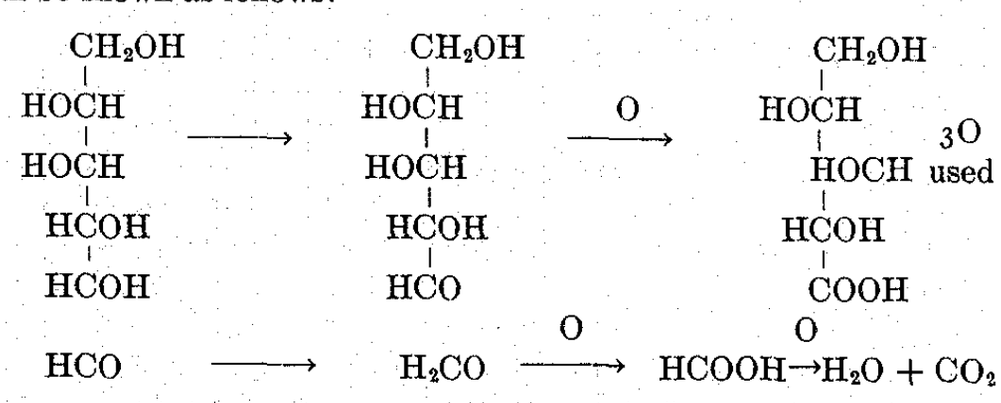
If this conception is correct, an increase in the alkalinity of the solution should favor 3,4 enediol formation. The products for this fission may be:

1. Oxidation of glyceric aldehyde to glyceric acid.
2. Further enolization of glyceric aldehyde and subsequent oxidation of the product to glycollic and formic acids.
3. Rearrangement of the glyceric aldehyde to form pyruvic aldehyde and then lactic acid.

Evans and others[3] have found that the amount of lactic acid formed is a function of the alkalinity and the temperature. Since lactic acid formation from glyceric aldehyde does not require any oxidation, this reaction would tend to lower the copper number for glucose. This has been verified by the experimental evidence illustrated in Fig. 1. These investigators used various concentrations of potassium hydroxide as their alkali.

This theory will largely account for all the results which have been obtained in this paper. It has been shown that gluconic acid will not reduce Fehling solution and that consequently the oxidation of the aldehyde group of the glucose molecule cannot take place first, as only one atom of oxygen would be used per molecule of glucose. Furthermore, Upson and Jensen obtained only 0.5 grams of gluconic acid from 200 grams of glucose, or 0.25% which is within experimental error. Obviously then, enolization must occur before oxidation.

The amount of oxygen that would be used by the splitting of a one, two enediol can be shown as follows:

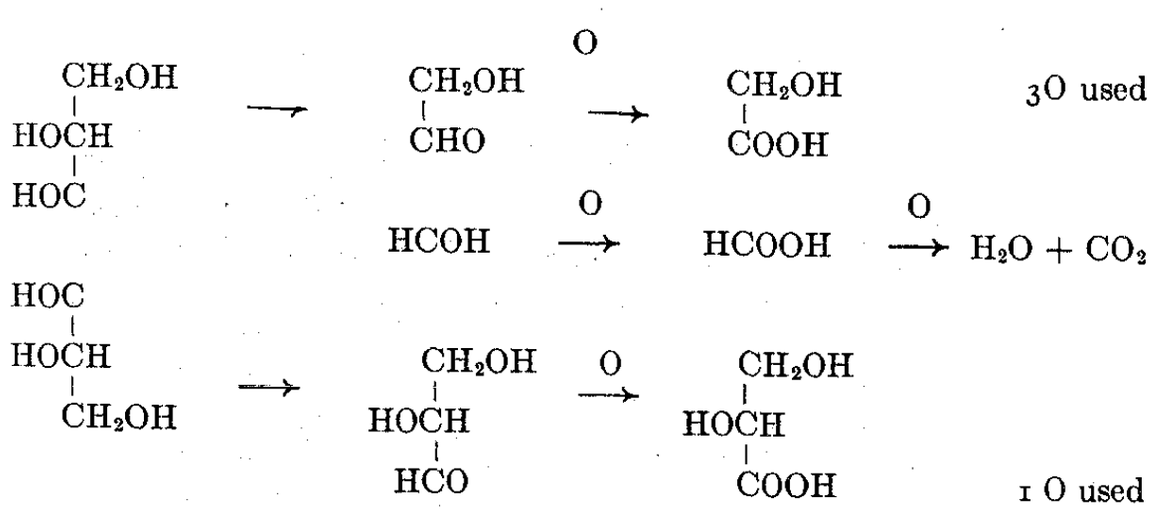


Thus if the entire molecule forms 1,2 enediol, and then splits, only three atoms of oxygen would be used and we have already seen that five may be used experimentally.

[1] J. Am. Chem. Soc., **48**, 195 (1926).
[2] J. Am. Chem. Soc., **47**, 3019 (1925).
[3] J. Am. Chem. Soc., **48**, 2665 (1926).

If the glucose forms the 2,3 enediol, and then oxidizes through erythrose and glyceric aldehyde to erythronic and glycollic acid, only two atoms of oxygen per molecule of glucose are needed. But Nef[1] has found that all tetroses (erythrose) give two molecules of a diose by splitting through the 2,3 enediol. This would give glycollic acid as the first oxidation product, three molecules being formed from one mole of glucose and three atoms of oxygen. But only three atoms of oxygen are thus accounted for. Apparently the glycollic acid is not oxidized to oxalic acid as might be expected. Neither Nef[2] nor Upson and his co-workers have obtained any oxalic acid when oxidizing glucose with alkaline copper solutions. Thus it seems that the primary alcohol group is not attacked by the weak oxidizing solutions. These workers have not obtained large quantities of glycollic acid in their experiments and if the molecule underwent 2,3 enolization, this acid would be the principal product formed. (Furthermore, no formic acid would be accounted for as Nef[3] stated that in no case was formic acid and a pentose formed from a hexose).

Only the 3,4 enolization remains as the source of any formic acid which is the principal product in weakly alkaline solutions. The direction of this reaction follows:



The only one of these three reactions which gives formic and glycollic acids is the first one. Here, the glyceric aldehyde undergoes a second enolization theoretically, but this has not been verified experimentally. One mole of formic acid should be formed for each mole of glycollic acid, and four atoms

[1] Ann, **376**, 1-119 (1910).

[2] In a later article, Ann., **403**, 204 (1914), Nef states that H_2O_2 or O_2 in alkaline solution of glucose forms these products.

[3] J. Am. Chem. Soc., **48**, 2667 (9926).

of oxygen be needed. Evidently, the oxidation of formic acid to give CO_2 and water also occurs thus accounting for the fifth oxygen. All of the investigators mentioned on the last few pages have reported the presence of CO_2 in these oxidations, which they stated came presumably from the oxidation of formic acid.

It is evident from these results that the amount of 3,4 enediol formation is always much greater than either of the others, although it is not clear just why this should be so. The equilibrium as suggested by Evans and others[1] is evidently shifted far to the right in very weakly alkaline solutions. The presence of the oxidizing agent at the time of the enolization may account for this. The formation of lactic acid in the more alkaline solutions with a consequent lowering of the copper number has already been indicated. The high values obtained by Soldiani's solution may be due to the fact that the alkalinity is too low for lactic acid formation, but sufficient to split the molecule into two trioses as indicated on the preceding page. The buffer action of carbonates may be responsible for this type of splitting as the alkalinity would be maintained constant for a considerable time.

Conclusions

In this paper, it has been shown that:

1. The use of alkaline copper solutions for the estimation of glucose is valueless because:

a. The amount of the oxidation is dependent on the alkalinity of the solution.

b. The method may be made to give any concordant results which one desires, using from one to five atoms of oxygen for each molecule of glucose.

2. It has been shown that solutions made alkaline by carbonates give higher copper numbers than those using free alkali. This result may be due to the buffer action of the carbonates, and an alkalinity too low to permit the formation of lactic acid.

3. The reducing action of the glucose molecule is *not* due to carboxyl formation from the carbonyl group as is commonly supposed; furthermore, the oxidation of the carbonyl to the carboxyl stabilizes the molecule and further oxidation does not occur. This precludes the formation of gluconic or saccharic acid as intermediate steps in the oxidation process.

4. The results agree with the theories proposed by Nef and his school for the formation by reducing sugars of enediols and subsequent fission, the nature of the enediol formation and splitting being dependent upon the alkalinity of the solution, and occurring before any oxidation of the glucose molecule.

5. The volumetric method of Bertrand is inaccurate for two reasons:

a. The asbestos mat or filter paper adsorbs some of the Fehling solution which cannot be removed by subsequent washing but which is removed by the acidified iron alum solution.

b. The ferric salts catalyze the oxidation of the adsorbed tartrates by the permanganate.

6. Iron salts can be employed under certain conditions, by using sodium fluoride to remove the excess ferric ions. This forms a complex of the formula Na_3FeF_6, which is unstable in solutions of 2.5% acidity or higher. Iron salts may also be used with sodium pyro-phosphate if the acidity is kept below 0.1%.

7. A new volumetric method for the estimation of glucose employing alkaline copper oxide is given by which it is possible to eliminate filtration. In this method, phospho-molybdic reagent is used to oxidize the cuprous oxide and the blue molybdenum color is titrated to a colorless end-point with permanganate, in the cold.

8. The alkaline copper oxide is a stronger oxidizing agent than the Fehling solution.

9. No experiments have been made to ascertain the effect of the presence of so-called non-reducing sugars on the determination of glucose under the new conditions.

Acknowledgment

Some professors give instruction; others give inspiration. A very few are capable of giving both and Professor W. D. Bancroft is one of these few. It has been a pleasure to work with him, to enjoy the clearness of his vision, the keenness of his perceptions, and the soundness of his judgment.

The author wishes to take this opportunity to thank the Pacific Mills for the endowment of a scholarship which he has enjoyed during the past year.

The author also wishes in this formal way to thank his wife, Marcella H. Amick, for her sympathetic understanding and cooperation throughout the course of this investigation.

Cornell University.

ELECTROMOTIVE FORCE OF THE CELL WITH TRANSFERENCE AND THEORY OF INTERDIFFUSION OF ELECTROLYTES

BY PAUL B. TAYLOR

A recent paper by Harned[1] on the thermodynamic behavior of individual ions is representative of the persistent attempts which have been made to establish a basis for the determination of the free energies of ions by means of the cell with transference, i.e., a cell containing a junction of two (different) electrolytes. The present analytical study leads to the conclusion that the EMF of the cell with transference is a function of free energies which are molecular only, that it can not possibly be manipulated to yield ionic free energies, and that the ionic free energy has not been thermodynamically defined. It is to be thought of rather as a purely mathematical device, which may indeed be employed safely with considerable freedom.

Electromotive Force of Cell with Transference as an Integral

In order to avoid a burdensome accretion of constant multipliers we shall measure concentration in reciprocal Faradays, i.e., the quantity of ionic species associated with one coulomb of electricity, per unit volume. Explicit reference to valence is thus generally avoided. We shall measure all free energies directly in joules per coulomb, i.e., in volts, and choose a temperature such that $RT = 1$. In the final formulae the factor RT/F may be restored and molalities divided by valence may replace concentrations; the formulae then become valid for customary units.

Consider the cell with transference:

$$(1) \mid m_1, m_2, --- m_i, --- \mid m'_1, m'_2, --- m'_i --- \mid (1)$$

The m's denote the concentrations of the various component ionic species in the left hand half of the cell, m''s those in the right. Odd subscripts denote cations, even anions, i denotes the typical ion of either sign. For definiteness the ion to which the electrodes are reversible, (1), has been chosen a cation.

Initially let the cell be one in which no transfer of solvent occurs either thru hydration or thru crystallization. Further let the concentrations in the two half cells differ by infinitesimals. Following the sign convention of Lewis and Randall the EMF of the cell, dE_{1t}, is given by

$$dE_{1t} = dF_1 - t_1 dF_1 + t_2 dF_2 - t_3 dF_3 \pm ---, \qquad (1)$$

where dF_i stands for the increase in free energy of ion i on passing from left to right, and t_i stands for its transference number, the fraction of current carried by ion i when the circuit is closed thru infinite resistance.

Now from a cell without transference of the type,

$$(1) \mid m_1, m_2, --- m_i --- \mid (2) \mid m'_1, m'_2, --- m'_i --- \mid (1),$$

[1] Harned: J. Phys. Chem., 30, 433 (1926).

whose observed EMF is dE_{12}, we have

$$dE_{12} = dF_1 + dF_2$$
$$dF_2 = dE_{12} - dF_1. \qquad (2)$$

Similar cells may be set up for each of the other anions with similar equations.

Likewise the cell

$$(1) \mid m_1, m_2, m_3 \text{ ---} \mid (3) \mid m'_1, m'_2, m'_3, \text{ ---} \mid (1),$$

whose EMF is dE_{13}, gives

$$dE_{13} = dF_1 - dF_3$$
$$dF_3 = dF_1 - dE_{13}; \qquad (3)$$

and similar equations hold for each of the other cations.

These values for dF_2, dF_3, --- being substituted, (1) becomes

$$dE_{1t} = dF_1 - t_1 dF_1 + t_2 (dE_{12} - dF_1) - t_3 (dF_1 - dE_{13}) \pm \text{---}$$
$$= dF_1 - (t_1 + t_2 + t_3 + \text{---}) dF_1 + t_2 dE_{12} + t_3 dE_{13} + \text{---}.$$

But

$$t_1 + t_2 + t_3 + \text{---} = 1.$$

Hence

$$dE_{1t} = t_2 dE_{12} + t_3 dE_{13} + \text{---}, \qquad (4)$$

and for a cell in which the concentrations vary continuously from one side to the other thru a finite range

$$E_{1t} = \int t_2 dE_{12} + \int t_3 dE_{13} + \text{---}. \qquad (5)$$

For the cell with electrodes reversible to an anion the same formula is arrived at, cation and anion subscripts being permuted. Hence, if 1 be taken to denote the ion of the electrode, odd subscripts to denote ions of like sign, even subscripts ions of contrary sign, (5) *becomes the general expression for the EMF of the cell with transference in terms of the corresponding cells without transference.*

When the number of ionic species is but two, the right hand member of (5) reduces to a single term, and will be recognized as a formula which has long been known.[1,2]

All terms in the ionic free energies have now been eliminated and E_{1t} expressed entirely in terms of transference numbers and EMF's of cells without transference, which latter may all be considered *molecular* free energies. If it be conceded that the transference numbers are not functions of the ionic free energies nor are the correction terms for transference of solvent (we shall presently prove both) our principal point is established, namely, that the EMF of a cell with transference is a function of molecular free energies only.

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[1] Helmholtz: Wied. Ann. 3, 201 (1878); Ber., 7, 27 (1882); Collected Papers 1, 840; 2, 979.

[2] MacInnes: J. Am. Chem. Soc., 37, 230 (1915).

Correction for Transference of Solvent

The expression for cell EMF is now to be corrected for the effect of transfer of solvent from one side of the cell to the other due to hydration of the ions and to solvent of crystallization. Let equations (1), (2), (3) be now the respective definitions of the quantities E_{1t}, E_{12}, E_{13}, — — —, and let the actual EMF's of the corresponding cells be denoted by italics, E_{1t}, E_{12}, E_{13}, — — —. Let s_i represent the quantity of solvent which due to crystallization with ion i is effectively transferred by ion i from left to right per unit of positive electricity flowing thru a cell from left to right. Let s_o represent that transferred due to hydration. Let dF_s represent the differential of increase in free energy of the solvent on passing from left to right.

The EMF of the cell with transference is now given by

$$dE_{1t} = dF_1 - t_1 dF_1 + t_2 dF_2 \pm - - - - (s_o + s_1) dF_s.$$

The EMF's of the cells without transference become

$$dE_{12} = dE_{12} - (s_2 + s_1)\, dF_s$$
$$dE_{13} = dE_{13} - (s_3 + s_1)\, dF_s.$$

Integrating, the EMF of the cell with transference becomes

$$E_{1t} = E_{1t} - \int (s_o + s_1)\, dF_s, \qquad (6)$$

or

$$E_1 t = \int t_2 dE_{12} + \int t_3\, dE_{13} + - - - + \int (-s_o - t_1 s_1 + t_2 s_2 + t_3 s_3 + - -) dF_s.$$

It is possible that other molecular species might be transferred in the same way as the solvent. In such case other terms similar to those in dF_s would need be added. With the inclusion of such terms equation (6) is exact. Obviously ionic free energies do not occur in these correction terms.

The transference numbers now remain to be examined. It is at least conceivable that dE_{1t} might be an exact differential and that E_{1t} might depend only on the initial and final concentrations, but theory[1] and experiment both show that it depends also on the manner in which the junction of the electrolytes is established. (One exception is the case of the cell with a single binary electrolyte; this case is too well understood to warrant any special attention.) In order to integrate (5) it is then impossible to avoid the necessity for expressing the molecular free energies, ionic mobilities, and concentrations thruout the cell in terms of a single variable. The distribution of these quantities depends on the manner of forming the junction, which may be in a variety of ways. One way is to connect the electrodes by a series of pools, each of which differs in composition from its neighbors by arbitrary small amounts. The distribution is then known and there is no theoretical impediment to the evaluation of E_{1t}. Plainly the transference numbers would not be functions of free energies. In particular the distribution may by this means be made that of Henderson (vid. Eq. (37)).

[1] Beatty: J. Am. Chem. Soc., **46**, 2211 (1924).

In all other cases the distribution of concentrations will depend not only on the manner of establishing and maintaining the junction but also on the specific ionic properties of diffusion. This latter condition we shall now express by exhibiting the concentrations as solutions of a set of differential equations.

Interdiffusion of Electrolytes

Consider two electrolytes in the process of interdiffusion in gravitational equilibrium. This is accomplished if the denser liquid is the lower, and forces of weight may then be neglected. It will be convenient to think of the cell as of unit cross section. Let us take the X axis vertical, origin arbitrary, and denote by m_i, the concentration of ionic species i at coordinate x and time t, by q_i its flux (quantity crossing unit section of the plane $x = c$ per unit time).

We define the mobility, u_i, by

$$u_i = q_i/(m_i \times (\text{force field})).$$

It must be sharply distinguished from the equivalent ionic conductivity, λ_i, which is defined by

$$\lambda_i = q_i/(m_i \times (\text{electrostatic field})).$$

If some of the ions are shielded from the full force of the electrostatic field the effective force is less than the electrostatic field, and λ is less than u. Since Ohm's law holds for electrolytes, λ is independent of the strength of the electrical field, and hence u is independent of the applied force (the more so that the forces in the present case are very small). λ and u may vary with the concentration.

We define the quantity, α_i, by

$$\alpha_i = \frac{\lambda_i}{u_i}.$$

It is called the degree of dissociation (not to be confused with the thermodynamic degree of dissociation or activity coefficient, γ). It is a measure of the fraction of (concentration $\times$ electrostatic field) which is effective in the flux. The effect may be due to incomplete dissociation of the ions but the actual cause is not implied.

Write the negative gradient of the ionic free energy

$$P_i = \frac{-dF_i}{dx}.$$

If now each ion diffused independently we should have the fluxes given by

$$q_i = u_i m_i P_i,$$

and the concentrations would be found as solutions of the equations of continuity

$$-\left(\frac{dm_i}{dt}\right)_x = \left(\frac{dq_i}{dx}\right)_t.$$

But since the total concentrations of cation and anion must remain everywhere equal there must be other forces besides the P's, say Q's. These Q's

are a set of mutual forces between the ions by which this equality is preserved. (Strictly the P's and Q's are forces per coulomb.) The fluxes are now

$$q_i = u_i m_i (P_i + Q_i ,) \tag{7}$$

and the equations of continuity

$$-\frac{dm_i}{dt} = \frac{d}{dx}\left[u_i m_i (P_i + Q_i)\right] . \tag{8}$$

Since the energy of the system is a function solely of the free energies, the Q's can do no work and hence must form a set of internal constraints in equilibrium. They are determined by the following conditions (9):

The flux of cation equals the flux of anion, or (distinguishing anions by subscript j)

$$i\sum u_i m_i (P_i + Q_i) = j\sum u_j m_j (P_j + Q_j) .$$

The Q's form a system of forces in equilibrium, or

$$i\sum m_i Q_i + j\sum m_j Q_j = o .$$

The rate of working of these forces is zero, or

$$i\sum u_i m_i (P_i + Q_i) Q_i + j\sum u_i m_i (P_i + Q_i) Q_i = o .$$

Also the concentration of cation equals that of anion, or

$$i\sum m_i = j\sum m_j .$$

We shall now divide the flux of each ionic species into two parts which we shall designate as the ionized and the unionized. We shall define the ionized portion of the flux as that portion which is affected to the full extent by a uniform impressed electric field. Any portion which is so affected is necessarily also affected to the full extent by a microscopic interionic field. Denoting it by subscript α we have for each ionic species

$$q_{i\alpha} = u_i m_{i\alpha} (P_i + Q_{i\alpha}) . \tag{10}$$

From the definition of α_i we have

$$m_{i\alpha} = \alpha_i m_i ,$$

and also now we have

$$-Q_{1\alpha} = -Q_{3\alpha} = --- = Q_{2\alpha} = Q_{4\alpha} = --- = Q_\alpha .$$

In exactly similar fashion we may now divide the unionized flux into a portion for which the Q's are equal and a remainder for which they are not. Denote the portion of the concentration so included by

$$m_{i\beta} = \beta_i m_i .$$

This subdivision may be repeated until the whole flux of all ions is partitioned into groups each with a common Q, or until completely associated molecules only remain, and within each molecule we must have the Q's equal.

From the solenoidal character of electrical induction it follows that equations (9) hold separately for each group and the fact that in each group the Q's are equal makes possible a solution.

The solution for the typical group is

$$Q_\alpha = \frac{u_1 m_{1\alpha} P_1 - u_2 m_{2\alpha} P_2 \pm - - -}{u_1 m_{1\alpha} + u_2 m_{2\alpha} + - - - -} . \tag{11}$$

Inserting the values of Q_α in (10) yields

$$q_{i\alpha} = u_i m_{i\alpha} \frac{u_1 m_{1\alpha} (P_i \mp P_1) + u_2 m_{2\alpha} (P_i \pm P_2) + - - -}{u_1 m_{1\alpha} + u_2 m_{2\alpha} + - - -} . \tag{12}$$

Here and elsewhere the upper sign is to be taken for i a cation, the lower i an anion.

But

$$P_i \mp P_1 = - \frac{dF_i}{dx} \pm \frac{dF_1}{dx} = - \frac{dE_{i1}}{dx}$$

$$P_i \pm P_2 = - \frac{dF_i}{dx} \mp \frac{dF_2}{dx} = - \frac{dE_{i2}}{dx} ,$$

and (12) becomes

$$- q_{i\alpha} = u_i m_{i\alpha} \frac{u_1 m_{1\alpha} dE_{i1} + u_2 m_{2\alpha} dE_{i2}}{(u_1 m_{1\alpha} + u_2 m_{2\alpha} + - -)\, dx} . \tag{13}$$

The equations of continuity becomes

$$\frac{dm_i}{dt} = - \frac{dq_{i\alpha}}{dx} - \frac{dq_{i\beta}}{dx} - - - -$$

$$= \frac{d}{dx} \left[u_i m_{i\alpha} \frac{u_1 m_{1\alpha} dE_{i1} + u_2 m_{2\alpha} dE_{i2} + - -}{(u_1 m_{1\alpha} + u_2 m_{2\alpha} + - - -)\, dx} + - - \right] . \tag{14}$$

Since the u's, E's, α's, β's $- - -$ are function only of (all) the m's, *the total of these equations for all species form the set of dynamical equations, the solutions of which together with the arbitrary boundary conditions in time and space completely determine the state of the system.*[1] In particular they determine the concentrations at every point.

Ionic Free Energies not unique

Since the ionic free energies, the F's have been eliminated from (14) they will be absent from any expression for the concentrations, the m's, which satisfies (14). It is permissible to say that any function from which the ionic free energies can be eliminated by substitution of molecular energies is a function of the latter and not of the former. We have already shown that ionic energies can enter the cell EMF only thru the transference numbers, and the transference numbers only thru the concentrations. Being absent from the concentrations they are then absent from both transference numbers and cell EMF. *The EMF of the cell with transference is thus a function of molecular free energies solely and is not a function of ionic free energies. It therefore can yield no information whatsoever concerning ionic energies.* In fact no thermo-

[1] We have restricted the system to one which varies in the X direction only. This restriction is removed by replacing d/dx by the Laplacian operator ∇.

dynamic information can be gained from a cell with transference which could not better be gained from a cell without transference. Conversely, within our present purview a knowledge of the ionic energies is never necessary for an account of the thermodynamics of electrolytes. Indeed, with the possible exceptions of single electrode potentials and rates of reaction there appears to be no occasion for the use of ionic free energies as experimental quantities but only as a mathematical device.

If any one ionic free energy in a solution be fixed, all the rest of the ionic free energies in that solution are determined thru the molecular energies. It now follows that for thermodynamic purposes we are at complete liberty to choose arbitrarily in each solution the free energy of any one ion, or more generally to set up for each solution any single arbitrary functional relation between the ionic energies (not a function of the molecular energies). In addition we may, of course, in any one solution choose arbitrarily every ionic energy. The ionic free energies thus determined have meaning only as they are referred to the arbitrary function but no thermodynamic inconsistencies will result from such procedure. This really puts into our hands a powerful tool for abridging computation. For instance we may take the free energy of one ionic species everywhere as zero and thus eliminate one term from a series; we may take the free energy of one cation equal to that one anion, or the total energy of cation equal to the total of anion.

An example of this use of partial energies is given in the paper cited of Harned's.[1] He there writes for the p.d. of the liquid junction (solvent transfer being neglected)

$$E_l = -\,i\sum \frac{RT}{v_i F}\int t_i d\ln a_i,$$

v_i being valence and a_i activity of ion i.

The value of the cell EMF in terms of E_l is

$$E_{lt} = ({}_2F_1 - {}_1F_1) + E_l\,,$$

where the F's are the free energies of the ion of the electrodes in the two half-cells. Harned evaluates E_{lt} from known data computing the two terms separately. To do this he postulates for one ion pair the relation

$$dF_K = dF_{Cl}.$$

The value of E_{lt} so computed is found to agree with the observed value; but this is not to be taken as a verification of the postulate, for he shows that another relation between dF_K and dF_{Cl} yields the same result, and we see from the foregoing that it would likewise be obtained on the basis of any relation whatsoever (subject to the sum of dF_K and dF_{Cl} being correct). The agreement is then to be taken as a verification of the formal correctness of his modification of the Henderson formula for the liquid junction p. d., E_l; it does not verify the numerical accuracy of this term in any absolute sense.

[1] J. Phys. Chem., **30**, 433 (1926).

Another instance of the successful arbitrary employment of ionic free energies is in the so called law of additivity of ionic free energies. This law is usually stated on the assumption that the free energy of K and Cl are always equal, but clearly it is just as correct if based on equality for any other two ions. It is indeed a *molecular law* and not ionic at all. However, insofar as the law is a fact it is only to be explained on the basis of an *ionic theory*, and the use of ionic free energies for such purposes is natural and desirable. The law of additivity is only approximate, but some universal function must exist which *will* give the free energies of each molecular species in any electrolyte. This will be a function of various quantities, one or more for each ionic species present, which quantities will be capable of experimental determination. It may be found useful to construct some subordinate function of these quantities and call it the ionic free energy, but until the universal function is found there is no occasion for the subordinate one.

Concentration Distribution across a Junction

Equations (14) will now be used to find the distribution of concentrations in the junction as ordinarily formed and the cell EMF for that distribution.

The treatment thus far has been rigorous. Application of the theory is hampered, however, by our ignorance of the quantities u and α, not to speak of β, etc. The old theory of Kohlrausch considered that the mobility, u, was constant at all concentrations for each ion and that the degree of dissociation, α, varied with the equivalent conductance, λ. There is much excellent modern evidence for considering that α is constant (unity) and that u varies.[1,2] The direct determination of the u's should be possible from the coefficients of diffusion, but the author is not aware of any recent use of such data.

We shall now restrict our consideration to the case of the Q's being equal, i. e.,

$$-Q_1 = - - - = Q_2 = - - - - = Q$$

This means at any one place in the solution each ionic species is affected to the same extent by the surrounding inter-ionic field. All species will then be affected equally by an externally impressed field, whence

$$\alpha_1 = \alpha_2 = - - - - = \alpha.$$

This may be called the case of equal ionization; and these relations will be assumed for the remainder of this paper. They are probably correct for all concentrations of strong electrolytes (as Debye has shown). The treatment here permits α to be different from unity (incomplete ionization) and to vary with the concentration.

The common value of Q which satisfies equations (9) is now satisfied by

$$-Q_1 = - - - - = Q_2 = - - - - = Q$$

$$Q = \frac{u_1 m_1 dF_1 - u_2 m_2 dF_2 \pm - - -}{(u_1 m_1 + u_2 m_2 + - - -)dx}. \qquad (15)$$

[1] Debye: Physik. Z., **24**, 185 (1923) etc.

[2] Onsager: Physik. Z., **27**, 388 (1926).

Cf. (11).

$$-q_i = u_i m_i \frac{u_1 m_1 (dF_i) \mp dF_1) + u_2 m_2 (dF_i \pm dF_2) + - -}{(u_1 m_1 + u_2 m_2 + - - -)\, dx} . \quad (16)$$

Cf. (12).

The equations of continuity (8) become

$$\frac{dm_i}{dt} = \frac{d}{dx} u_i m_i \frac{u_1 m_1 (dF_i \mp dF_1) + u_2 m_2 (dF_i \pm dF_2) + - -}{(u_1 m_1 + u_2 m_2 + - - -)\, dx} . \quad (17)$$

Cf. (14).

These equations will now be integrated for the following conditions. Consider that the two electrolytes of the half cell are initially brought together over the plane $x = o$ at $t = o$, that there are no other forces applied than the P's and Q's, and that the electrolytes extend away into a region that is not sensibly affected by the diffusion, i. e., to a physical infinity. It is not necessary that the initial physical distribution be exactly as described, for it is the property of diffusion that states initially different become in the course of time more and more alike.

Denote the concentration of ionic species i in the left hand half-cell (at $-\infty$) by M_i in the right hand (at $+\infty$) by M'_i. Write

$$\overline{M}_i = \tfrac{1}{2} (M_i + M'_i)$$

$$\Delta_i = \tfrac{1}{2} (M'_i - M_i) .$$

(7) may now be put in the form

$$q_i = -\int_{-\infty}^{x} \frac{dm_i}{dt} dx = u_i m_i (P_i \pm Q) . \quad (18)$$

It is now necessary to know the P's and u's as functions of the m's. The first approximation is

$$u_i = \text{a constant} ,$$

$$F_i = \frac{1}{v_i} \log m_i .$$

v_i is the valence (T has been chosen so that RT is unity). Hence

$$P_i = -\frac{dm_i}{v_i m_i dx} ,$$

$$Q = -\frac{\frac{u_1}{v_1} dm_1 - \frac{u_2}{v_2} dm_2 \pm - - -}{(u_1 m_1 + u_2 m_2 + - - - -)\, dx} . \quad (19)$$

The equation of continuity (17) becomes

$$-\frac{dm_i}{dt} = \frac{d}{dx} \left[-\frac{u_i}{v_i} \frac{dm_i}{dx} \pm u_i m_i \frac{\frac{u_1}{v_1} dm_1 - \frac{u_2}{v_2} dm_2 \pm - - -}{(u_1 m_1 + u_2 m_2 + - - -) dx} \right] . \quad (20)$$

In the special case that the u/v's are all equal to a common constant C^2, Q vanishes and (20) becomes

$$\frac{dm_i}{dt} = -\frac{d}{dx}\left(u_i m_i P_i\right) = C^2 \frac{d^2 m_i}{dx^2}.$$

The solution is well known[1]

$$m_i = \triangle_i \int_0^z \frac{2}{\sqrt{\pi}} e^{-(z/C)^2} \frac{dz}{C} + \overline{M}_i, \qquad (21)$$

where $z = \frac{x}{2\sqrt{t}}$.

The integral is the Gaussian probability function of zero order, Π_o, in terms of which

$$m_i = \triangle_i \Pi_o\left(\frac{z}{C}\right) + \overline{M}_i.$$

The solution will now be extended to the case that the u's are different. Since the u's are constant it follows from the principle of dynamical similitude that x and t can enter with the u's an expression for the m's only as functions of x^2/t. For the u's are of the dimensions t/x^2 and a change in the *units* of length and time cannot alter the m's. (the dimensions of the m's may be taken as the third fundamental unit.) Hence it must always be possible to write the m's as functions of z as defined above.

(21) yields (for the u's equal)

$$\frac{dm_i}{dt} = \triangle_i \frac{2}{\sqrt{\pi}} e^{-(z/C)^2} \frac{dz}{C\,dt}.$$

The solution for the u's not equal is gotten by considering that this may be altered at time t into any other permissible function whatsoever (consistent with the boundary conditions) by applying a correction factor (if $\triangle_i \neq o$). The Weierstrassian differential so obtained is

$$\frac{dm_i}{dt} = \triangle_i \left[\frac{2}{\sqrt{\pi}} A_i + 2B_i \frac{z}{c_i} + \frac{4}{\sqrt{\pi}} C_i \left(\frac{z}{c_i}\right)^2 + - -\right] e^{-(z/c_i)^2} \frac{dz}{c_i dt}.$$

The numerical coefficient of the nth term is $2/\Gamma\left(\frac{n+1}{2}\right)$.

The constants c_i, A_i, B_i, C_i, — — — — remain to be determined.

The integral is

$$m_i = \triangle_i \left[A_i \Pi_o\left(\frac{z}{c_i}\right) + B_i \Pi_1\left(\frac{z}{c_i}\right) + C_i \Pi_2\left(\frac{z}{c_i}\right) + - -\right] + \overline{M}_i. \qquad (22)$$

The Π's are the Gaussian functions of higher order defined by

$$\Pi_n(z) = \frac{2}{\Gamma\left(\frac{n+1}{2}\right)} \int_0^z z^n e^{-z^2} dz.$$

[1] Byerly: "An Elementary Treatise on Fourier's Series, etc.," p. 83.

Those of even order are odd functions, of odd order even. At $\pm\infty$ the odd function become ± 1, the even $+1$.

The values of the constants, C_i, A_i, B_i, $---$, will be gotten by writing the m's as solutions of equations (18). For the left hand member we have by (22)

$$q_i = -\int_{-\infty}^{x} \frac{dm_i}{dt}\,dx = -\Delta_i \int_{-\infty}^{x} \left[\frac{2}{\sqrt{\pi}} A_i + 2B_i \frac{z}{c_i} + \frac{4}{\sqrt{\pi}} C_i \left(\frac{z}{c_i}\right)^2 + -- \right] e^{-(z/c_i)^2} \frac{dz}{c_i dt}\,dx .$$

From the definition of z

$$\frac{dz}{dt}\,dx = -\frac{z}{\sqrt{t}}\,dz .$$

The integral is then

$$\frac{\Delta_i c_i}{\sqrt{t}} \int_{-\infty}^{x} \left[\frac{2}{\sqrt{\pi}} A_i \frac{z}{c_i} + 2B_i \left(\frac{z}{c_i}\right)^2 + -- \right] e^{-(z/c_i)^2} \frac{dz}{c_i} .$$

We break the integral into two terms

$$\int_{-\infty}^{x} = \int_{-\infty}^{o} + \int_{o}^{x} ,$$

and obtain

$$q_i = \Delta_i \frac{c_i}{\sqrt{t}} \left[\frac{A_i}{\sqrt{\pi}} \left(\Pi_1\left(\frac{z}{c_i}\right) - 1 \right) + \frac{\sqrt{\pi} B_i}{2} \left(\Pi_2\left(\frac{z}{c_i}\right) + 1 \right) + -- \right] . \quad (23)$$

The right hand member of (18) is from (20)

$$q_i = -\frac{u_i}{v_i} \frac{dm_i}{dx}$$

$$\pm u_i m_i \frac{\dfrac{u_1 dm_1}{v_1} + \dfrac{u_3 dm_3}{v_3} + ---- - \dfrac{u_2 dm_2}{v_2} - \dfrac{u_4 dm_4}{v_4} ---}{(u_1 m_1 + u_2 m_2 + --- \qquad) dx} .$$

Writing the m's in terms of (22),

$$q_i = -\frac{u_i}{v_i} \Delta_i \left(\frac{1}{\sqrt{\pi}} A_i + B_i \left(\frac{z}{c_i}\right) + --- \right) e^{-(z/c_i)^2} \frac{1}{c_i \sqrt{t}}$$

$$\pm u_i \left[\Delta_i \left(A_i \Pi_o \left(\frac{z}{c_i}\right) + -- \right) + \overline{M}_i \right] \times$$

$$\frac{\dfrac{u_1 \Delta_1}{v_1} \left[\dfrac{A_1}{\sqrt{\pi}} + B_1 \left(\dfrac{z}{c_1}\right) + -- \right] e^{-(z/c_1)^2} \dfrac{1}{c_1 \sqrt{t}} \pm ---}{u_1 \left[\Delta_1 \left(A_1 \Pi_o \left(\dfrac{z}{c_1}\right) + --- \right) + \overline{M}_1 \right] + ---} . \quad (24)$$

Comparing the two expressions for q_i, (23) and (24), we see that the factor $\sqrt{t}$ cancels and any set of coefficients (A_1, B_1, $---$ A_2, B_2, $-----$) which is a solution at one time will yield a solution at all times.

To secure the first n coefficients (23) and (24) may be expanded in power series in z and the coefficients of like powers equated. In order for the end concentrations to be given correctly the coefficients must satisfy the additional equations

$$A_i + B_i + C_i + --- = 1 \qquad (25)$$
$$A_i - B_i + C_i - --- = 1$$

The c_i's are also unknowns to be determined. In a system of i ionic species there will then be i (n + 2) equations to be satisfied by i (n + 1) variables. By deriving a separate solution for each side of the origin only one of (25) need be satisfied at a time, and the number of equations equals the number of variables. As the number of terms is increased the two solutions approach each other. Equation (22) then gives the distribution of the ionic species thruout the junction for the assumed force laws and boundaries.

Since the m's will be given as functions of a single variable, z, we may eliminate z and write the m's as functions of a single m independent of x or t. As the time could enter the expression for cell EMF only thru the m's, it follows that *the EMF of the cell is independent of the time.* This is due to the fact that an initial distribution has been chosen which may be written as a function of z. Indeed the above method can be applied only in such a case. If we had chosen an initial distribution which required x as an independent variable we should not have been able to eliminate either x or t from m. The EMF of such a cell would vary with time approaching as a limit the EMF of the solved case. It is then seen that *the correct way to set up a cell with transference is to form a junction with initially a sharp boundary between the electrolytes and thereafter to let them interdiffuse undisturbed.*

The rule is varied by the experiments of Cummings and Gilchrist[1] with large junctions. The unsteady p. d. observed by them when the junction was made thru a narrow capillary was presumably due to the equipotential surfaces being no longer planes, as is postulated in the present development.

First Order Solution in Detail

The expansion of (22) as far as first order terms will now be developed. In this case the m's are given as odd functions plus constant terms. The B's, C's, etc. become zero, the A's are unity; and since both of (25) are thereby satisfied the same solution applies to both sides of the origin. Values of c_i will be obtained by equating (23) and (24). Neglecting all powers of z and with $\sqrt{\pi t}$ cancelled, they appear thus

$$-\triangle_i c_i = -\frac{u_i \triangle_i}{v_i \quad c_i} \pm u_i \overline{M}_i \frac{\frac{u_1 \triangle_1}{v_1 \quad c_i} - \frac{u_2 \triangle_2}{v_2 \quad c_2} \pm ---}{S}$$

[1] Cummings and Gilchrist: "Trans. Faraday Soc., 9, 174 (1913).

where $S = u_1\bar{M}_1 + u_2\bar{M}_2 + ---$. The upper sign with i is for i a cation, lower i an anion. Transposing,

$$\mp \frac{S\,\triangle_i}{\bar{M}_i}\left(\frac{c_i}{u_i} - \frac{1}{v_i c_i}\right) = \frac{u_1\,\triangle_1}{v_1\ c_1} - \frac{u_2\,\triangle_2}{v_2\ c_2} \pm ----$$

$$-\frac{S\,\triangle_1}{\bar{M}_1}\left(\frac{c_1}{u_1} - \frac{1}{v_1 c_1}\right) = \frac{u_1\,\triangle_1}{v_2\,c_2} - \frac{u_2\,\triangle_2}{v_2\,c_2} \pm ---$$

(26)

Substracting,

$$\frac{\triangle_1}{\bar{M}_1}\left(\frac{c_1}{u_1} - \frac{1}{v_1 c_1}\right) = \pm\frac{\triangle_1}{\bar{M}_i}\left(\frac{c_i}{u_i}\frac{1}{v_i c_i}\right). \tag{27}$$

Similarly

$$\frac{\triangle_2}{\bar{M}_2}\left(\frac{c_2}{u_2} - \frac{1}{v_2 c_2}\right) = \mp\frac{\triangle_i}{\bar{M}_i}\left(\frac{c_i}{u_i} - \frac{1}{v_i c_i}\right).$$

Put

$$p_i \equiv \frac{c_i}{u_i} - \frac{1}{v_i c_i}.$$

Then from (27)

$$\frac{2u_1}{v_1 c_1} = \mp u_1 p_i \frac{\bar{M}_1\triangle_i}{\bar{M}_i\triangle_1} + \sqrt{u_1^2 p_i^2 \frac{\bar{M}_1^2\triangle_i^2}{\bar{M}_i^2\triangle_1^2} + \frac{4u_1}{v_1}}.$$

$\frac{2\,u_2}{v_2 c_2}$ is a similar expression with the sign of p_i reversed.

Substituting these in (21)

$$\mp\frac{2p_i\triangle_i S}{\bar{M}_i} = \mp u_1 p_i\triangle_i\frac{\bar{M}_1}{\bar{M}_i} + \delta_1\sqrt{u_1^2p_i^2\triangle_i^2\frac{\bar{M}_1^2}{\bar{M}_i^2} + \frac{4u_1\triangle_1^2}{v_1}}.$$

$$\mp u_2\ p_i\ \triangle_i\frac{\bar{M}_2}{\bar{M}_i} - \delta_2\sqrt{u_2^2p_i^2\triangle_i^2\frac{\bar{M}_2^2}{\bar{M}_i^2} + \frac{4u_2\triangle_2^2}{v_2}} \mp ---$$

where δ_i is ± 1 as $\triangle_i$ is positive or negative. This may be simplified into

$$\mp p_i\triangle_i S = \delta_1\sqrt{u_1^2\bar{M}_1^2\triangle_i^2p_i^2 + 4u_1\triangle_i^2\bar{M}_i^2/v_1}$$

$$-\delta_2\sqrt{u_2^2\bar{M}_2^2\triangle_i^2p_i^2 + 4u_2\triangle_2^2\bar{M}_i^2/\ v_2} \pm ---$$

(28)

The equation is now in shape for numerical solution for p_i, from which c_i may be obtained. The radicals are numerically positive.

In a system of two ionic species of the same valence (28) yields

$$\frac{1}{c_1^2} = \frac{1}{c_2^2} = \frac{v}{2}\left(\frac{1}{u_1} + \frac{1}{u_2}\right)$$

in agreement with more elementary methods.

Extension to Mobilities and Activity Coefficients variable

It will now be shown how the given solution of the dynamical equations (18) may be extended to cover a more general force law that that which has been first assumed. The form of the simple law may be maintained in the general law by writing

$$F_i = \frac{1}{v_i} \log \gamma_i m_i$$

where γ_i, the activity coefficient, is a variable function of the concentrations Since the F's are subject to an arbitrary function the γ's are also subject to one.

If the γ's for all ions may be chosen so as to vary in a common ratio from one solution to another and the λ's also vary in another common ratio, we may write

$$\gamma_i = \eta K_i \lambda_i \qquad (29)$$

where K_i is a constant of the species and η is an unspecified function of the solution common to all ions. (29) would hold in certain other cases also. In binary electrolytes no test of (29) can be made unless η is restricted to unity. In that case it leads to a relation between molecular free energies and λ/λ_o ratios formally different from that commonly stated,[1] but which fits the experimental data equally well and has as much theoretical justification. No data are available on ionic conductivities in mixed electrolytes but the measurements by Bray and Hunt[2] of total conductivities indicate a similar behavior there. (29) is probably good to the same extent that the conductance-viscosity ratio is a measure of the van't Hoff coefficient.

(29) may be put in the form

$$\frac{{}_2\gamma_i}{{}_1\gamma_i} = \frac{{}_2\eta\ {}_2\lambda_i}{{}_1\eta\ {}_1\lambda_i} \qquad (29a)$$

the left hand subscripts referring to two different solutions. As only the ratio ${}_2\eta/{}_1\eta$ is needed, ${}_1\eta$ may be taken as unity. (29) and (29a) though stated in ionic terms, really involve only molecular free energies.

With this force law we have

$$dF_i = \frac{d(\eta \lambda_i m_i)}{v_i \eta \lambda_i m_i}.$$

Since

$$u_i = \frac{\lambda_i}{\alpha_i}$$

and we are assuming

$$\alpha_1 = \alpha_2 = \text{---} = \alpha,$$

$$u_i m_i = \frac{\lambda_i m_i}{\alpha}$$

$$u_i m_i\, dF_i = \frac{d(\eta \lambda_i m_i)}{v_i \alpha}.$$

[1] Taylor: "A Treatise on Physical Chemistry" **2**, 757.
[2] Bray and Hunt: J. Am. Chem. Soc., **33**, 781 (1911).

We now remove the restriction that u_i be constant and as a second approximation write

$$\eta\lambda_i m_i = \frac{\gamma_i m_i}{K_i} = a_i m_i + b_i \qquad (30)$$

$$d(\eta\lambda_i m_i) = a_i dm_i .$$

a_i and b_i are constants and are determined from the presumably known values of the m's, γ's and λ's in the two half cells, the two values of η being chosen so as to make equations (29) be satisfied as nearly as possible. From (30) now follows

$$u_i m_i = \frac{1}{\alpha\eta}(a_i m_i + b_i)$$

$$u_i m_i dF_i = \frac{a_i dm_i}{v_i \alpha\eta} .$$

By (15) we now have

$$Q = -\frac{\frac{a_1}{v_1}dm_1 - \frac{a_2}{v_2}dm_2 \pm ----}{[(a_1m_1 + b_1) + (a_2m_2 + b_2) + ---]\,dx}$$

and the equation of continuity (8) becomes

$$-\frac{dm_i}{\alpha\eta dt} = \frac{d}{\alpha\eta dx}\left[\frac{a\,dm_i}{v_i\alpha\eta dx} \pm (a_i m_i + b_i)\frac{\frac{\alpha_1}{v_1}dm_1 \pm ---}{[(\alpha_1 m_1 + b_1) + ---]\,\alpha\eta dx}\right]. \qquad (31)$$

Comparing this with (20) we see that it is the same equation with $\alpha\eta dt$ replacing dt, αdx replacing dx, $m_i + \frac{b_i}{a_i}$ replacing m_i, and a_i replacing u_i. The solution of (20) for m_i, namely (22), is then a solution of (31) for $m_i + \frac{b_i}{a_i}$ $\overline{M}_i + \frac{b_i}{a_i}$ replacing $\overline{M}_i$, and z being now defined as $\frac{x}{2}\sqrt{\frac{\alpha\eta}{t}}$. Since z is the independent variable it is not necessary here to know anything about α or η. If b_i/a_i be subtracted from each side of the equation we regain the solution for m_i itself, exactly as given by (22) a_i replacing u_i. *Equation (22) is then a quite general solution, since it provides for the continuous variation of conductances and activities between practically their exact values in the two limits.*

In the case of a species present thruout the cell it is convenient to consider it as composed of two species one from each half-cell. This is a device which must be used with caution, but is here permissible. We now have for every species $\triangle_i/\overline{M}_i = \pm 1$. The variation of activity and conductivity as given in (29) and (30) is seen to be preserved. The b's vanish and

$$a_i = \eta\lambda_i ,$$

η and λ_i being the values of η and λ_i appropriate to species i in the half-cell in which it occurrs in finite concentration.

Equations (19)-(28) are in general valid for the extended force laws (29), (30), a_i replacing u_i. If the γ's are constants, η is unity and λ_i replaces u_i.

The Junction Potential Difference

The distribution of concentrations thru the liquid junction having been determined with more or less exactness the problem remains of finding the cell EMF. It may be remarked that the two are distinct problems and the assumptions made in determining the concentrations need not now be continued. It was necessary to assume various functional relations between the variables in order to solve the set of simultaneous differential equations. But once the distribution of m's is found the integration of dE_{it} can be effected by graphical methods, even when the functional relations are not given but only series of data. However the bulk of the integration may be performed analytically by Henderson's[1] formula, which will now be extended to apply to the force law of (29).

Returning to equation (1) (and neglecting transfer of solvent) it is seen that if dF_1 be interpreted as the differential of the sum of the electrode potentials the remainder is the differential of the junction p. d., E_l. As a definition we write

$$E_l = -\int t_1 dF_1 + \int t_2 dF_2 \pm - - -$$

Since $\int dF_1$ *is entirely arbitrary,* E_l *is equally arbitrary and of itself without significance.* However the integration of dE_l is tantamount to the integration of dE_{it}, for the latter is easily gotten by adding on $\int dF_1$.

The transference numbers are given rigorously by

$$t_i = \frac{\lambda_i m_i}{\lambda_1 m_1 + \lambda_2 m_2 + - -}.$$

Write

$$W = \lambda_i m_1 + \lambda_2 m_2 + - - -$$
$$dY = \lambda_1 m_1 dF_1 - \lambda_2 m_2 dF_2 \pm - - -.$$

Then rigorously

$$dE_l = -dY/W. \qquad (32)$$

On the basis of (29) alone

$$\lambda_i m_i dF_i = \frac{d(\eta \lambda_i m_i)}{v_i \eta}.$$

Write

$$Y_H = \frac{\eta \lambda_1 m_1}{v_1} - \frac{\eta \lambda_2 m_2}{v_2} \pm - - -$$
$$W_H = \eta(\lambda_1 m_1 + \lambda_2 m_2 + - - -).$$

Then the value of dE_l resulting from (29) is

$$dE_{lH} = \frac{-dY_H}{W_H}. \qquad (33)$$

The approximation is now introduced that (k being a constant)

$$dY_H = k\, dW_H. \qquad (34)$$

[1] Henderson: Z. physik. Chem., **59**, 118 (1907); **63**, 325 (1908). Planck's formula (Wied, Ann., **39**, 161 (1890); **40**, 561 (1890)) does not apply to the junction here considered. It applies to a junction in which the distribution of concentrations is maintained steady by artificial means.

The integral of (33) for a temperature of T°K is then

$$E_{1H} = -\frac{RT}{F}\frac{{}_2Y_H - {}_1Y_H}{{}_2W_H - {}_1W_H}\ln\frac{{}_2W_H}{{}_1W_H}. \qquad (35)$$

The subscripts $_1$ and $_2$ refer to the values of W and Y in the left and right hand half-cells respectively.

(35) will be put into more familiar form.

Write

$$U = \lambda_1 m_1 + \lambda_3 m_3 + - -$$
$$V = \lambda_2 m_2 + \lambda_4 m_4 + - -$$
$$U' = \lambda_1 v_1 m_1 + \lambda_3 v_3 m_3 + - - -$$
$$V' = \lambda_2 v_2 m_2 + \lambda_4 v_4 m_4 + - - -$$

where the m's now denote *molalities* as commonly defined. (35) is now

$$E_{1H} = -\frac{RT}{F}\frac{{}_2\eta({}_2U - {}_2V) - {}_1\eta({}_1U - {}_1V)}{{}_2\eta({}_2U' + {}_2V') - {}_1\eta({}_1U' + {}_1V')}\ln\frac{{}_2\eta({}_2U' + {}_2V')}{{}_1\eta({}_1U' + {}_1V')}. \qquad (36)$$

$_1\eta$ and $_2\eta$ are the values of η which best satisfy equations (29) in the two half-cells. The λ's are the actual specific conductivities in the two half-cells and may be different in $_1U$ from what they are in $_2U$.

Equation (36) is an extension of Henderson's formula and differs from it by the presence of the factors $_2\eta$, $_1\eta$. It permits the specific conductivities to vary continuously between their exact limiting values in the two half-cells and employs activity coefficients which are also variable and quite approximately correct in many cases. By Henderson the formula was derived for infinite dilution, i. e., for constant λ and γ.

Lewis and Sargent[1] showed experimentally that for finite dilution it naturally gave better results if (constant) values of λ were used appropriate to the true concentration rather than λ_o.

The present derivation differs also from Henderson's in the avoidance of some of the crudity in the concentration distribution known as his "uniform mixing assumption." This assumption is replaced by (34), which is the correct first approximation whatever the true distribution may be.

If η be constant (34) reduces to

$$\frac{dm_1}{\triangle m_1} = \frac{dm_2}{\triangle m_2} = - - - - -, \qquad (37)$$

from which the simple Henderson formula may be obtained. It may be shown that (37) can not be strictly true unless

$$\lambda_1 = \lambda_2 = - - - -,$$

and its departure from the truth is the greater the greater the differences between the λ's of the various ions. In this regard (34) and (36) are also in error and to a similar extent, as is, of course, Henderson's original formula.

Equation (36) is then in error in two respects: it is based on an energy relation (29) which is not exact, and the distribution of concentrations thru-

[1] Lewis and Sargent: J. Am. Chem. Soc., **31**, 363 (1909).

out the junction as given by (34), or (37), is not correct. In terms of E_{IH} the exact value of E_I is

$$E_I = E_{IH} + \int \left(\frac{I}{W_H} - \frac{I}{W} \right) dY. \tag{38}$$

W and W_H are values of W and W_H corresponding to equal values of Y and Y_H.

Harned has shown how to get the part of the second term which corrects for the variations of the γ's (the λ's being considered constant). His method may be modified to give the correction for the variations of the γ's from the values given by (29).

Application to a Specific Concentration Cell

We shall now give a specific example of the application of the theory which has been developed. Consider the cell at 25° C

$$Cl \mid HCl\ .1M \mid KCh\ .1M \mid Ch\ .$$

Ch stands for chlorine from the right hand half cell.

It might be thought that the concentration of chlorine would remain constant thruout the cell and that (34) might hold strictly. It may be shown however that such a distribution would introduce a set of constraints which would not balance, and the true distribution must be found by (22). This will now be done and the results then used to find the correction term of (38).

Since the correction term to the cell EMF due to the departures of the concentrations from those given by (34) is a small one due to large differences in the u's, approximate (constant) values of the u's will suffice. η is taken unity. Since only ratios are needed, we may write as u's the ratios of the λ's to one another. Only ratios of concentrations are needed, so for convenience they will be increased twenty fold. The data are then:

	Left		Right	
	H	Cl	K	Ch
u	4.84	1	1	1
$\frac{\Delta}{M}$	−1	−1	1	1
	1	1	1	1

The first step is to solve (28) for pK, i. e., p for K ion.

$$-7.84p_K = -\sqrt{4.84^2p_K^2 + 4 \times 4.84} + \sqrt{p_K^2 + 4} + \sqrt{p_K^2 + 4} - \sqrt{p_K^2 + 4}$$

$$p_K = .341$$

The c's are found from (37). For convenience we use for the 1/c's the ratios of the reciprocals.

	H	Cl	K	Ch
c	1.525	1.185	1.185	.844
1/c	.7772	1.000	1.000	1.404

(22) appears as

$$m_i = \Delta_i \Pi_o \left(\frac{z}{c_i} \right) + 1.$$

In Table I are given the solutions for a series of points thruout the junctions. The values of Π_0 are taken from the tables of Jahnke and Emde. The 6th column gives the total concentration of cation, m_+, the 7th of anion, m_-. The 8th gives the excess of cation concentration above 2, the 9th that of anion above 2. The 10th is the difference of anion and cation concentrations.

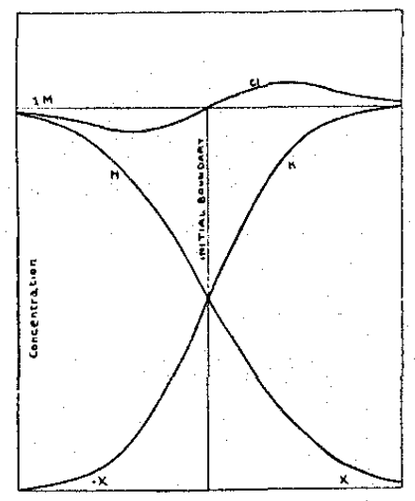


FIG. 1
Concentration Distribution at .1 M HCl KCl Junction

The values e_+, e_-, measure the departures of the true concentration distribution from that which would be given by (34) or (37). The values of $m_- - m_+$ give the error caused by the retention of but two terms in the expansion of (22). Since m_+ must equal m_- the true values probably lie between m_+ and m_- as found. The values of e_+ then give a lower limit to the departures. We accordingly accept the m_+ values in favor of the m_- as the concentration of total chlorine.

The computation is continued in Table II. Columns 2 and 3 give the values of Y and W. Here

$$Y = \lambda_1 m_1 - \lambda_2 m_2 \pm ----,$$

the m's of the preceding table being employed. In column 4 is given the value of W_H corresponding to a value of Y_H equal to Y given in 2, equation

TABLE I

1	2 x20	3	4	5	6	7	8	9	10
z	m_K	m_{Ch}	m_H	m_{Cl}	m_+	m_-	e_+	e_-	$m_- - m_+$
$-\infty$	.0000	.0000	2.0000	2.0000	2.0000	2.0000			
−2.0	.0047	.0001	1.9720	1.9953	1.9767	1.9954			
−1.0	.1573	.0471	1.7283	1.8427	1.8856	1.8898			
− .6	.3961	.2335	1.4904	1.6039	1.8865	1.8374			
− .2	.7773	.6913	1.1739	1.2227	1.9512	1.9140			
.0	1.0000	1.0000	1.0000	1.0000	2.0000	2.0000	.00	.00	.00
.2	1.2227	1.3087	.8261	.7773	2.0488	2.0860	.05	.09	.04
.6	1.6039	1.7665	.5096	.3961	2.1135	2.1626	.11	.16	.05
1.0	1.8427	1.9529	.2717	.1573	2.1142	2.1102	.11	.11	.00
2.0	1.9953	1.9999	.0280	.0047	2.0233	2.0046	.02	.00	−.02
∞	2.0000	2.0000	.0000	.0000	2.0000	2.0000	.00	.00	.00

(37) being employed. In column 5 is given $D = 1/W_H - 1/W$; in column 6 the sums of D's corresponding to equal positive and negative values of z, that is, to Y's which differ by equal amounts from the mean value 3.8400.

The values in column 6 plotted as ordinate against Y as abscissa then give the correction integral

$$\int_{7.68}^{0}\left(\frac{1}{W_H}-\frac{1}{W}\right)dY.$$

This is found to be $-.0130$, twice as many points being used as are shown in the tables. For 25°C this must be multiplied by .0257, (RT/F), giving the correction term $-.33$ mv. The error in Henderson's formula due to the use

TABLE II

1	2	3	4	5	6
z	Y	W	W_H	$D=1/W_H-1/W$	D_z-D_{-z}
$-\infty$	7.6800	11.6800	11.6800	.00000	
−2.0	7.5724	11.5258	11.5724	−.00035	
−1.0	6.6367	10.4079	10.6367	−.00207	
− .6	5.7231	9.4961	9.7231	−.00246	
− .2	4.5077	8.4101	8.5077	−.00137	
.0	3.8400	7.8400	7.8400	.00000	.00000
.2	3.1723	7.2699	7.1732	.00186	.00049
.6	1.9567	6.1839	5.9567	.00616	.00370
1.0	1.0433	5.2721	5.0433	.00862	.00655
2.0	.1076	4.1542	4.1076	.00273	.00238
∞	.0000	4.0000	4.0000	.00000	.00000

of (34) is thus seen to be very slight. However, it is an error which does not decrease with dilution, if the relative concentrations be maintained. Increasing the relative H concentration in one half-cell will produce a large correction term. The correction may amount to as much as 10 mv. but such cells would not be of practical importance. It might also be found larger if the free energy function were different from the one here used.

The principal part of the cell EMF will now be obtained by computation of E_{1H} as given by (36). The following data are available: [1, 2, 3, 4].

	Left		Right	
γ_{HCl}	.814		.803	
γ_{KCl}			.794	
λ_H	324.4	λ_{Cl} 66.0	λ_K 63.9	λ_{Cl} 65.1

The remaining data necessary to determine ${}_2\eta/{}_1\eta$ are inferred as follows: λ_K/λ_{Cl} is taken constant thruout the cell. $d\gamma_{HCl}/d\lambda_{HCl}$ is taken to have the same value from pure .1M HCl to pure .1M KCl that it has in varying

[1] Conductivities, Noyes and Falk: J. Am. Chem. Soc., **34**, 454 (1912).
[2] Activity coefficients, Lewis and Randall: "Thermodynamics," p. 362.
[3] Activity coefficient of .0M HCl in .1M KCl, Harned: J. Am. Chem. Soc., **48**, 326 (1926).
[4] n_0 in HCl, Noyes: "Conductivity of Aqueous Solutions," p. 327.

concentrations of pure HCl. Comparison of data from the sources mentioned yields for pure HCl the quite constant value

$$\frac{d\gamma_{HCl}}{d\lambda_{HCl}} = 193.$$

From this λ_{HCl} in pure KCl is found to be 388.3. Similarly is found in pure KCl

$$\frac{d\gamma_{KCl}}{d\lambda_{KCl}} = 105,$$

from which γ_{KCl} in pure HCl is found to be .811. We take

$$\gamma_K = \gamma_{Cl}$$

and the complete data now appear:

	Left			Right		
	H	K	Cl	H	K	Cl
γ	.904	.901	.901	.902	.891	.891
λ	324.4	64.8	66.0	323.2	63.9	65.1

The ratio $_2\eta/_1\eta$ may now be computed from (29a). From the H data it is 1.0015 and from the K and Cl 1.0026. We adopt 1.002 for η_2, as η_1 may always be taken as unity.

These data in (36) now yield E_{1H} as 28.21 mv. Applying the correction term $-.33$ mv according to (38) we obtain the junction p. d., E_1, as 27.88 mv. The sum of the electrode p. d.'s is given by

$$-.05915 \log \frac{.901}{.891} = -.29 \text{ mv.}$$

Hence the cell EMF is 27.6 mv. The observed value according to Lewis, Brighton and Sebastian[1] is 27.8 mv. This is very satisfactory agreement, but it must be remembered that part of the data rests on conjecture. Any reasonable values for these uncertain data lead to nearly the same result however. MacInnes and Yu[2] also measured this cell using a flowing junction, and found its EMF 26.78 mv. The reason for the disparity is unknown, though the present theory does not necessarily apply in every particular to such a junction.

The simple Henderson formula assuming constant λ's and γ's reduces in this case to

$$.05915 \log \frac{\lambda_{HCl}}{\lambda_{KCl}}$$

and yields a cell EMF of 28.45 mv. The values are compared below.

E M F of Cell, Cl | .1M HCl | .1M KCl | Cl

Computed		Observed	
Henderson	Taylor	L,B&S	M&Y
28.4 mv.	27.6	27.8	26.78

[1] Lewis, Brighton and Sebastian: J. Am. Chem. Soc., **39**, 2245 (1917).
[2] MacInnes and Yu: J. Am. Chem. Soc., **43**, 2563 (1921).

The correction term for transfer of solvent (equation 6) has been estimated and found negligible.

pH Numbers from Cells with Transference

In the preceding pages we have considered the problem of computing the EMF of the cell with transference from given data. We should rather consider: Given the EMF of the general cell with transference, what information can be inferred? Owing to the complexity of such a cell it appears that very little can be inferred with certainty. In particular the determination of pH numbers by such a cell is not the simple thing it is sometimes assumed, for the cell EMF depends not only on the acid activity but also on the activity of every molecular species in the cell and mobility of every ion. If these are sufficiently well known to be allowed for, the acid activity is likely to be sufficiently well known not to need measurement.

The discussion ought to have made plain the futility of trying to eliminate the liquid junction p.d. either analytically or experimentally. The liquid junction must be regarded as a convenient grouping of terms in the expression for cell EMF and of itself without physical significance. Thus the KCl bridge should be examined in the light of the EMF of the whole cell, or we may use a half cell with hypothetical electrode, e. g.,

$$H \mid KCl\ (sat.) \mid HR \mid H.$$

The EMF by (1) is

$$E_{Ht} = \int t_K dE_{HK} + \int t_{Cl} dE_{HCl} + \int t_R dE_{HR}.$$

This may also be written

$$\int (t_K + t_{Cl})\, dE_{HCl} + \int t_R dE_{HR} - \int t_K dE_{KCl}.$$

If the concentration of HR is low t_K and t_{Cl} tend to the value .5 thruout the range of E's which contribute materially to the integral and t_R is small. *Thus the cell EMF approaches the difference between the change in free energy of HCl and one half the change of that of KCl.* How close is the approach can only be told by computing out E_{Ht}. In many cases it will be within a few millivolts, but the presence of other ions in the cell, as is commonly the case, will complicate matters, and cells are known in which E_{Ht} is even of opposite sign from the above described limit.

If we wish to postulate

$$F_K = F_{Cl}$$

these quantities, F_K and F_{Cl}, tend to cancel, and we have

$$E_{Ht} \doteq \int (t_K + t_{Cl} + t_R)\, dF_H + \int t_R dF_R.$$

This is less than the change in hydrogen ion free energy, $\triangle F_H$, by

$$\int t_H dF_H - \int t_R dF_R.$$

dF_H is approximately equal to dF_R but t_H is four or five times t_R. If a sufficient number of cells of known composition were studied it would be possible to form an idea of what the correction to a given observed E_{Ht} would be to reduce it to $\triangle F_H$.

The determination of pH numbers directly from cell EMF's in those cases where they are known to give satisfactory results is of course not to be questioned, but their uncritical use in all cases regardless of the constitution of the electrolyte can only be deplored.

The applicability of the various formulae which have been considered may now be summarized. There are two main types of junction available:

(1) a series of junctions, the gradations in concentration being made to conform to Eq. (37) or to (34). A poor approach to this is to stir the electrolytes together. The cell EMF may then be computed in ascending order of accuracy by the simple Henderson formula, the author's formula, Harned's method, a graphical correction for residual errors. No correction for concentration distribution is needed.

(12) the single, sharp, plane, large junction, which must be neither stirred nor shaken. The three formulae apply less closely than to the first junction, so that the concentration distribution should be found by equation (22) and a correction term computed, as has been exemplified. Better still is a graphical integration to correct for any variations in λ's and γ's otherwise unconsidered made on the basis of the true distribution. The second junction makes more laborious computation but gives an EMF nearer the limit desired for pH number.

It is my pleasure to acknowledge indebtedness to Professor Herbert S. Harned for many fruitful discussions concerning the subject of this paper.

Summary

I. An integral has been derived for the EMF of the general cell with transference, Eq. (5), including the effect of solvent transfer, (6).

II. The differential equation of diffusion of electrolytes, (14), is derived rigorously, and is shown to depend on molecular free energies only and to be independent of ionic free energies.

III. From this it is shown that the EMF of the cell with transference is independent of ionic free energies, and that ionic free energies may always be chosen in each solution to satisfy any single arbitrary function (not a function of the molecular free energies) without thermodynamic error.

IV. A method is given for finding the distribution of concentrations thruout a junction under conditions sufficiently broad to make it generally applicable.

V. Henderson's formula for liquid junction p. d's. is extended to provide for variable mobilities and activity coefficients. The formula is an approximation and it is shown how to get the correction as a graphical integral.

VI. The theory applied to the tenth normal HCl | KCl cell gives much better results than have been obtained heretofore by the simple Henderson formula.

VII. The bearing of these results on pH determination are considered.

Morgan Physical Laboratory,
University of Pennsylvania.

GIBBS ON ADSORPTION

BY WILDER D. BANCROFT

There is a footnote on adsorption by Gibbs,[1] which seems not to have received the attention which it deserves.

"If liquid mercury meets the mixed vapors of water and mercury in a plane surface, and we use μ_1 and μ_2 to denote the potentials of mercury and water respectively, and place the dividing surface so that $\Gamma_1 = 0$, i.e., so that the total quantity of mercury is the same as if the liquid mercury reached this surface on one side and the mercury vapor on the other without change of density on either side, then $\Gamma_{2(1)}$ will represent the amount of water in the vicinity of this surface, per unit surface, above that which there would be, if the water-vapor just reached this surface without change of density, and this quantity which we may call the quantity of water condensed upon the surface of the mercury) will be determined by the equation $\Gamma_{2(1)} = -d\sigma/d\mu_2$. (In this differential coefficient as well as the following, the temperature is supposed to remain constant and the surface of discontinuity plane. Practically, the latter condition may be regarded as fulfilled in the case of any ordinary curvatures.)

"If the pressures in the mixed vapors conform to the laws of Dalton, we shall have for constant temperature $dp_2 = \gamma_2 d\mu_2$, where p_2 denotes the part of the pressure in the vapor due to the water-vapor, and γ_2, the density of the water-vapor. Hence we obtain $\Gamma_{2(1)} = -\gamma d\sigma/dp_2$. For temperatures below 100° centigrade, this will certainly be accurate, since the pressure due to the vapor of mercury may be neglected."

If we postulate that water vapor is described by the simple gas law, and if we write x for the amount of water vapor adsorbed per unit surface of mercury, the first equation becomes

$$x = -d\sigma/RT\ d\log p_2.$$

If the variation of the surface tension at constant temperature is proportional to the change in the amount adsorbed, we can write

$$d\sigma/dx = -nRT.$$

Substituting in the preceding equation, we have

$$n dx/x = RT\ d\log p$$

which integrates to Freundlich's equation

$$x^n = kp.$$

In so far as Gibbs is right this is the condition for the absolute accuracy of the Freundlich equation. If $d\sigma/dx$ is not a constant for constant temperature, the Freundlich equation will not hold. Furthermore, for the first time, we learn the physical significance of the exponent n. With a liquid adsorbent, n is a measure of the change of the surface tension with the amount adsorbed.

[1] "Scientific Papers," **1**, 235 (1906)

The data of Patrick[1] on the adsorption of mercurous sulphate from solution by mercury can be represented moderately well by Freundlich's equation, Table I.

TABLE I

Formula $x^{5.6}=kc$ where x = amount adsorbed; c = equilibrium concentration, both in millimols per liter; k = 0.0046 (459).

x	c found	c calc
0.105	0.000	0.001
0.190	0.020	0.020
0.261	0.054	0.118
0.315	0.315	0.321
0.358	0.692	0.692

The third figure is not as much out as it appears to be. Changing the amount adsorbed from 0.261 to 0.240–1, a change of less than ten percent would bring the concentration up to 0.75–0.74 and would make it fit exactly with the formula. This point lies off the smooth curve as Patrick has drawn it and is therefore in error to some extent.

Patrick gives a curve and not the data for surface tension against equilibrium concentration. Guessing at the surface tension values from the curve and plotting them against the amounts adsorbed gives pretty close to a straight line. The real curve cannot be a straight line because the straight line, when prolonged, does not come anywhere near the surface tension of pure mercury for zero adsorption. This means that the Freundlich equation with these constants only holds over a portion of the adsorption curve, which is all that anybody expects of the Freundlich equation.

Patrick's data for salicylic acid, picric acid, and new fuchsine cannot be represented with any satisfactory degree of accuracy by the Freundlich equation, though they give a smooth curve, indicating adsorption. The data of Iredale[2] for the adsorption of methyl acetate vapor by mercury cannot be used because he did not determine the amounts adsorbed. Years ago, Freundlich[3] started from exactly the same equation, but substituting concentrations for pressures. He wrote $u = -\frac{c}{RT}\frac{\delta\sigma}{\delta c}$, where u is what I have called x. He wished to get the adsorption in the surface of a solution and postulated an empirical formula $(\sigma_M - \sigma_L) = sc^{1/n}$ where σ_M is the surface tension of the pure liquid, σ_L the surface tension of the solution, and s is a constant. From this he deduced $d\sigma/dc = -\frac{s}{n}c^{\frac{1}{n}-1}$ and $u = \frac{s}{nRT}c^{1/n} = \alpha c^{1/n}$, where α is a new constant. This deduction rests of course on the validity of the empirical equation connecting the surface tension and the con-

[1] Z. physik. Chem., **86**, 545 (1914).
[2] Phil. Mag. (6) **45**, 1088 (1923).
[3] "Kapillarchemie," 51, 65, 75 (1909).

centration. This is admittedly not accurate. Since σ_M is a constant at constant temperature, the empirical equation can of course be written[1]

$$\frac{\sigma_M - \sigma_L}{\sigma_M} = s_1 c^{1/n}$$

On p. 61 of the English translation, Freundlich says: "A theoretically well-founded formula which gives the connexion between σ and c does not at present exist. Its deduction, for instance, from the van der Waals theory of liquids is no simple matter. We only need to consider that it has hardly been found possible to represent a single property of a solution—say the compressibility or density—by means of this theory. Too little is indeed known about the extent to which the attractive force acting between unlike molecules (the quantity a_{12} of van der Waals) must be taken into account, and the attractive forces a_1 and a_2 between like molecules; and, further, we know too little about the degree and nature of hydration. In other words, the lyotropic properties of solutions cannot yet be expressed quantitatively, and referred to simple quantities. An empirical formula, which gives the relation between σ and c very satisfactorily, is due to von Szyszkowski.[2] It runs thus:

$$\Delta = \frac{\sigma_M - \sigma_L}{\sigma_M} = b \log\left(\frac{c}{c} + 1\right)$$

when σ_M and σ_L have the significance previously given and b and c are constants."

While this is true, it resembles the flowers that bloom in the spring because one can eliminate practically all the difficulties to which Freundlich refers, by sticking to the case, cited by Gibbs, of the adsorption of a gas by mercury.

The connection between Freundlich's relation and the one I have used is quite simple. If we assume that Freundlich's empirical equation and his adsorption equation hold simultaneously for small changes of surface tension, then $\sigma_M - \sigma_L = sc^{1/n} = k_1 x$, this is equivalent to $d\sigma/dx =$ constant, which is the condition, according to Gibbs, for Freundlich's equation being accurate.

The relation between surface tension and adsorption is for a liquid adsorbent and of course we are usually more interested in adsorption of a gas or a solution by a solid. So far, I have not been able to find any definite statement in Gibbs that a similar relation holds for solids; but he certainly implies that there is a great similarity between the two cases.[3]

"We have hitherto treated of surfaces of discontinuity on the supposition that the contiguous masses are fluid. This is by far the most simple case for any rigorous treatment, since the masses are necessarily isotropic both in nature and in their state of strain. In this case, moreover, the mobility of the masses allows a satisfactory experimental verification of the mechanical con-

[1] Freundlich: "Colloid and Capillary Chemistry," 66 (1927).
[2] Z. physik. Chem., **64**, 385 (1908).
[3] "Scientific Papers," 1, 314 (1906).

ditions of equilibrium. On the other hand, the rigidity of solids is in general so great, that any tendency of the surfaces of discontinuity to variation in area or form may be neglected in comparison with the forces which are produced in the interior of the solids by any sensible strains, so that it is not generally necessary to take account of the surfaces of discontinuity in determining the state of strain of solid masses. But we must take account of the nature of the surfaces of discontinuity between solids and fluids with reference to the tendency toward solidification or dissolution at such surfaces, and also with reference to the tendencies of different fluids to spread over the surfaces of solids.

"Let us therefore consider a surface of discontinuity between fluid and a solid, the latter being either isotropic or of a continuous crystalline structure, and subject to any kind of stress compatible with a state of mechanical equilibrium with the fluid. We shall not exclude the case in which substances foreign to the contiguous masses are present in small quantities at the surface of discontinuity, but we shall suppose that the nature of this surface (i.e. of the non-homogeneous film between approximately homogeneous masses) is entirely determined by the nature and state of the masses which it separates, and the quantities of the foreign substances which may be present. The notions of the *dividing surface*, and of the *superficial densities* of energy, entropy, and several components, which we have used with respect to surfaces of discontinuity between fluids (see pages 219 and 224), will evidently apply without modification to the present case. We shall use the suffix $_1$ with reference to the substance of the solid, and shall suppose the dividing surface to the determined so as to make the superficial density of this substance vanish. The superficial densities of energy of entropy, and of the other component substances may then be denoted by our usual symbols (see page 235),

$$\epsilon_{s(1)},\ \eta_{s(1)},\ \Gamma_{2(1)},\ \Gamma_{3(1)},\ \text{etc.}$$

Let the quantity σ be defined by the equation

$$\sigma = \epsilon_{s(1)} - t\eta_{s(1)} - \mu_2\Gamma_{2(1)} - \mu_3\Gamma_{3(1)} - \text{etc.}, \qquad (659)$$

in which t denotes the temperature, and μ_2, μ_3, etc., the potentials for the substances specified at the surface of discontinuity," p. 314

Equation (659) is nearly the same as equation (514).

$$d\sigma = -\eta_{s(m)}\,dt - \Gamma_{2(1)}\,d\mu_2 - \Gamma_{3(1)}\,d\mu_3 - \text{etc.}, \qquad (514)$$

from which Gibbs started in deducing the relation between surface tension and adsorption for liquid absorbents. Of course, there is a difference, as pointed out by Gibbs.

"As in the case of two fluid masses (see page 257), we may regard σ as expressing the work spent in forming a unit of the surface of discontinuity—under certain conditions, which we need not here specify—but it cannot properly be regarded as expressing the tension of the surface. The latter quantity depends upon the work spent in *stretching* the surface, while the quantity σ depends upon the work spent in *forming* the surface. With respect to perfectly fluid masses, these processes are not distinguishable, unless

the surface of discontinuity has components which are not found in the contiguous masses, and even in this case (since the surface must be supposed to be formed out of matter supplied at the same potentials which belong to the matter in the surface) the work spent in increasing the surface infinitesimally by stretching is identical with that which must be spent in forming an equal infinitesimal amount of new surface. But when one of the masses is solid, and its states of strain are to be distinguished, there is no equivalence between the stretching of the surface and the forming of new surface.

"This will appear more distinctly if we consider a particular case. Let us consider a thin plane sheet of a crystal in a vacuum (which may be regarded as a limiting case of a very attenuated fluid), and let us suppose that the two surfaces of the sheet are alike. By applying the proper forces to the edges of the sheet, we can make all stress vanish in its interior. The *tensions* of the two surfaces are in equilibrium with these forces, and are measured by them. But the tensions of the surfaces, thus determined, may evidently have different values in different directions, and are entirely different from the quantity which we denote by σ, which represents the work required to form a unit of surface by any reversible process, and is not connected with any idea of direction.

"In certain cases, however, it appears probable that the value of σ and of the superficial tensions will not differ greatly. This is especially true of the numerous bodies which, although generally (and for many purposes properly) regarded as solids, are really very viscous fluids. Even when a body exhibits no fluid properties at its actual temperature, if its surface has been formed at a higher temperature, at which the body was fluid, and the change from the fluid to the solid state has been by insensible gradations, we may suppose that the value of σ coincided with the superficial tension until the body was decidedly solid, and that they will only differ so far as they may be differently affected by subsequent variations of temperature and of the stresses applied to the solid. Moreover, when an amorphous solid is in a state of equilibrium with a solvent, although it may have no fluid properties in its interior, it seems not improbable that the particles at its surface, which have a greater degree of mobility, may so arrange themselves that the value of σ will coincide with the superficial tension, as in the case of fluids," p. 315.

Freundlich[1] considers that we are forced to assume a surface tension for a solid. "It is the mobility of liquids which enables us to recognize and measure their surface tension, but when we come to consider the interfaces of solid substances we encounter quite different conditions. Here the particles suffer mutual displacement with great difficulty, so that we cannot recognize the surface tension directly or measure it. Nevertheless it is found expedient to assume a surface tension of solids against a gaseous space. . . . Just as the increased vapour pressure of minute drops is related to the surface tension of liquids, so we may also connect the phenomena depending on the increased

[1] "The Elements of Colloidal Chemistry," 37.

vapour pressure of minute crystals with a surface tension for crystalline solids. We would therefore, on the basis of these observations, postulate such a surface tension for solids.

"A few phenomena may still be mentioned which can be explained on this hypothesis. Since tension tends to reduce the surface to a minimum, it should also tend to round off the sharp corners and edges of a crystal. Such crystals with rounded edges and corners are actually known. If, for instance, we heat a piece of metal to a high temperature which is still appreciably below the melting-point, surface tension may begin to overcome the rigidity of the individual crystals constituting the metal, the so-called crystallites, which then become rounded at the edges and corners. Surface tension is also the cause of recrystallization, in which the small crystals unite to larger ones at such temperatures below the melting-point."

Liquids spread on solids apparently just as they do on liquids and a slight excess may draw up into single drops in the two cases. A thin film of gold leaf becomes granular when heated, unquestionably as a result of surface tension. The melting-point could be considered as the temperature at which the surface tension overwhelms the crystalline forces. So far as we now know, the adsorption by liquids, amorphous solids, and crystalline solids is similar in nature. The theory of peptization postulates a change of surface tension with adsorption. All the phenomena point to the fact that we have a change of surface tension or of some equivalent property when adsorption occurs, regardless whether the adsorbing agent is a crystalline solid or a liquid. We are therefore justified, at least for the present, in applying the conclusions from the Gibbs equation to the case of adsorption by solids.

The general conclusions of this paper are:

1. From the work of Gibbs it follows that the necessary and sufficient criterion for the applicability of the Freundlich equation to the case of the adsorption of a gas by a liquid, in which the gas is practically insoluble, is that the change of the surface tension is proportional to the change of adsorption.

2. The exponent n in the Freundlich equation is a measure of the change of the surface tension with the adsorption in the case of a liquid adsorbent.

3. It seems probable that the necessary and sufficient criterion for the applicability of the Freundlich equation to the case of the adsorption of a gas by a solid is that the change of the surface tension or of some equivalent property is proportional to the change of adsorption.

4. In so far as conclusion 3 holds, conclusion 2 can be extended to cover the case of a solid adsorbent.

Cornell University.

THE PHOTOCHEMICAL DECOMPOSITION OF HYDROGEN PEROXIDE SOLUTIONS[1]

BY F. O. RICE AND M. L. KILPATRICK[2]

The photochemical decomposition of hydrogen peroxide is of interest in that it is one of the reactions deviating markedly from Einstein's Law of the Photochemical Equivalent. Henri and Wurmser[3] studied the photochemical decomposition of hydrogen peroxide solutions in monochromatic light, in the region between 2060 and 2800Å. Upon calculating the energy absorbed per molecule decomposed they found it much smaller than the quantum, and not increasing with the frequency of the light absorbed. On the average, the absorption of one quantum of light energy by a solution 0.04 N in hydrogen peroxide was followed by the decomposition of 100 molecules. Kornfeld[4] found that with decreasing concentration of hydrogen peroxide the photochemical yield decreased from 80 molecules per quantum in 0.5 N solution (two per cent peroxide) to 24 in 0.02 N (0.07 per cent).

Much study has been made of the effect of added substances[5] upon the velocity of decomposition. Organic compounds which absorb light in the ultra-violet, in the region in which hydrogen peroxide absorbs, retard the photochemical decomposition. An outside screen of the inhibiting substance is less effective, however, than is the inhibitor in direct contact with the peroxide. Diactinic inorganic compounds inhibit the reaction to different degrees. As Anderson states, bases are excellent inhibitors, acids good, and neutral chlorides and bromides fair. In the presence of sulfuric acid, an inhibitor, Kornfeld obtained photochemical yields as low as seven molecules per quantum, the yield for a solution 0.05 N in hydrogen peroxide and 0.1 N in sulfuric acid.

It occurred to one of us that motes, which catalyze the thermal decomposition of hydrogen peroxide solutions,[6] may also accelerate the photochemical decomposition, and that mote-free solutions of hydrogen peroxide may decompose at a rate not deviating greatly from that required by the Law of the Photochemical Equivalent. The following work shows that the former of these suppositions is justified.

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[1] Contribution from the Chemical Department of the Johns Hopkins University.

[2] Abstracted from the thesis of M. L. Kilpatrick presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy of the Johns Hopkins University.

[3] Henri and Wurmser: Compt. rend., **156**, 1012 (1913); **157**, 126 (1913).

[4] Kornfeld: Z. wiss. Phot., **21**, 66 (1921).

[5] Mathews and Curtis: J. Phys. Chem. **18**, 166, 521 (1914); Tian: Ann. Phys., (9) **5**, 248 (1916); Kailan: Z. physik. Chem., **98**, 495 (1921); Kornfeld: Z. wiss. Phot., **21**, 66 (1921); Anderson and Taylor: J. Am. Chem. Soc., **45**, 650, 1210 (1923).

[6] Rice and Reiff: Jour. Phys. Chem., **31**, 1352 (1927).

Experimental Part

Dust-free water was prepared by the method of Martin,[1] which consists of distilling a volatile liquid, in a closed and evacuated system, from one bulb to another without allowing it to boil at any time, pouring the liquid back into the distilling bulb, and repeating until the distillate in the receiving bulb appears free from motes when examined in an intense beam of light against a dark background. Water was siphoned from the receiving bulb to the quartz reaction vessel through a tube sealed into the receiving bulb. With more complicated apparatus than that used by Martin, it was often difficult to obtain dust-free water, as many as 20 distillations and rinsings being insufficient. It was also noticed that gentle shaking increased the number of motes in the water. Somewhat accidentally, it was found that apparatus which had been thoroughly melted in the process of construction gave dust-free water after two or three distillations, and thereafter the receiving bulb and connecting tubes of new distillation apparatus were always melted before use. Melting almost to the point of collapse of the vessel is necessary for the production of a surface which does not readily yield motes. In this connection a statement by Kenrick, Gilbert and Wismer[2] may be quoted: "That there is an apparently inexhaustible supply of detachable motes at the surface of glass vessels which are not removed in the preparation of mote-free water by distillation has been proved by Mr. Garrard in this laboratory."

Before a study of the photochemical decomposition of hydrogen peroxide could be undertaken, it was necessary to prepare a quantity of inhibitor-free peroxide. The preparation and concentration of hydrogen peroxide solutions are described in an earlier paper.[3] The reacting solution was prepared by adding hydrogen peroxide from a pipette to dust-free water in the quartz reaction vessel. The dust content of the original peroxide was therefore diluted. In addition to the dust from the hydrogen peroxide, some dust was introduced in transferring the water. However, examination showed that the so-called "dust-free" solution always contained many less motes than did a control solution which was made up from the same peroxide and from laboratory distilled water. It was estimated that the dust-free solution contained one-third or one-fourth as many motes as the control solution.

In each experiment, the relative rates of decomposition of a dust-free and a dusty solution of hydrogen peroxide were measured. No attempt was made to keep conditions strictly comparable from experiment to experiment; the distance from the lamp to the solutions, the current and voltage at which the lamp operated, and the temperature of the solutions, were different in different cases. In a single experiment, however, the dust-free and the dusty solution were subjected to as nearly the same treatment as possible. They were of the same concentration, and prepared from the same peroxide. Equal volumes of the two solutions were contained in quartz flasks of the same shape and capacity.

[1] Martin. J. Phys. Chem., **24**, 478 (1920); Martin and Lehrman: **26**, 75 (1922).
[2] Kenrick, Gilbert and Wismer: J. Phys. Chem., **28**, 1297 (1924).
[3] Kilpatrick, Reiff and Rice,: J. Am. Chem. Soc., **48**, 3019 (1926).

The source of ultra-violet light was one of two quartz-mercury vapor "Uviarc" lamps from the Cooper-Hewitt Company, one of the horizontal type, the other of the vertical. Both operated on the 110 volt d. c. circuit. The series resistance was adjusted to give an arc voltage of 55-60, and a corresponding current of 5.0-5.5 amperes. In order to prevent the heating of the reacting solutions, a copper screen through which ran a stream of water was placed between the solutions and the lamp. Quartz windows in the screen, opposite each other, allowed light to pass through to the solutions. When such a screen was used, the temperature of the solutions never rose more than a degree above the temperature of the room. A preliminary experiment showed that two portions of a solution of hydrogen peroxide in quartz flasks placed side by side on the quartz window above the lamp received practically equal amounts of light energy from the lamp, as measured by their rates of decomposition.

TABLE I

Exp't.	Percentage H_2O_2	cc. O_2/min. from dusty sol'n	cc. O_2/min. from dust-free sol'n	Ratio	Fall in titre per 3cc. dusty sol'n	Fall in titre per 3cc. dust-free sol'n	Ratio
I	3.6	1.7	.55	3.1:1			
II	3.6	2.2	.52	4.2:1			
III	3.6				21	6.3	3.1:1
IV	2.6	.51	.19	2.7:1	21	7.5	2.8:1

Rates of decomposition were measured gasometrically, by recording the rates of evolution of oxygen, and were confirmed in most cases by initial and final titration of the solutions with potassium permanganate. The solutions were not shaken or stirred, since high-speed stirring or shaking would have swept many motes into the dust-free solution from the walls of the vessel. It was found that the rates of evolution of oxygen from the unstirred solutions furnish true relative rates of decomposition after some 20cc. of gas have been given off from the dust-free solution.

Removal of a portion of the dust reduced the rate of decomposition to a third or a fourth the rate of decomposition of the control solution, as is shown in Table I. In Experiments (1) and (2) the solutions were prepared from hydrogen peroxide made from sodium peroxide and sulfuric acid; in Experiments (3) and (4), from Merck's "Superoxol, Reagent Grade," which is certified to contain no inhibitor.

The solutions prepared by adding peroxide to water transferred from the receiving bulb to the reaction vessel necessarily contain motes. Attempts were made to obtain cleaner solutions by distilling hydrogen peroxide into dust-free water in the quartz receiving bulb of the distillation apparatus, but due to decomposition the peroxide distilled with ebullition and in most cases the results were little different from those of Table I. A concentrated solution of peroxide, prepared in a somewhat similar way, decomposed very little when exposed to the lamp, and a description of this experiment is given in detail.

A quartz bulb of 50cc capacity was connected through a quartz to pyrex seal to a condenser and pyrex flask; the quartz bulb was then heated to melting so as to present a smooth surface. Water was then distilled from the pyrex bulb to the silica bulb repeatedly by Martin's method until the water in the silica bulb was free from motes; dust-free air was then allowed to enter the apparatus and the dirty water in the pyrex bulb was poured out. The clean water in the silica bulb was also poured out via the pyrex bulb which thus received a thorough rinsing with clean water. Eighty-seven percent hydrogen peroxide was then drawn into the pyrex bulb and a portion was distilled into the quartz bulb. The distillate contained a few very fine, hair-like particles; it appeared, however, far more free from motes than any solution hitherto prepared. The quartz bulb was then cut off from the apparatus just above the quartz-to-pyrex seal. The dust-free solution, and a control solution of the original peroxide, in a second 50cc quartz bulb, were exposed to light from the horizontal lamp. In three hours, over 300 cc of oxygen were given off from the dusty solution, and one cubic centimeter from the dust-free.

In sampling the dust-free material for analysis, the solution was vigorously shaken. Examination showed that the shaking had introduced motes, and it was thought worth while to determine the new rate of decomposition. Oxygen was given off from the solution at a constant rate, which amounted to 6.2 cc. per hour. The rate of evolution of oxygen from the control was 110 cc. per hour; these rates are in the ratio of 18 to one.

Discussion and Summary

Measurements by Henri and Wurmser, and Kornfeld, show that many molecules of hydrogen peroxide are decomposed upon the absorption of one quantum of light energy. Their work was done with solutions of hydrogen peroxide in water which contained motes. We have found that solutions of hydrogen peroxide in dust-containing and in dust-free water decompose at very different rates. Other things being equal, we have found that the rate of decomposition is roughly proportional to the dust content. By removing portions of the dust, we have obtained solutions decomposing from one-third to some value less than one-eighteenth as fast as the control or dust-containing solutions. Therefore it is to be expected that quantitative measurements of the rate of decomposition of dust-free solutions of hydrogen peroxide, absorbing known amounts of light energy, would show that this reaction deviates much less from the Law of the Photochemical Equivalent than is at present believed.

Baltimore, Md.

92-52

A STUDY OF THE STRUCTURAL CHANGES IN AMORPHOUS MATERIALS. SILICA GEL

BY W. A. PATRICK, J. C. W. FRAZER AND R. I. RUSH*

Introduction

Many experiments[1] have been carried out in which the adsorption of various vapors and liquids by silica gel has been studied, and much has been said in regard to the structure of silica gel. On the other hand, very few experiments have been conducted in which the effect of temperature on the structure of the gel has been studied. Van Bemmelen,[2] Berl and Urban,[3] and others have carried out some work along this line but no very definite conclusions have been drawn.

The object of this investigation was to obtain a more definite knowledge of the structural changes in silica gel when heated, and to propose a mechanism by which these changes take place.

Preparation of Materials

Pure silica gel was prepared as follows: One part of a solution of sodium silicate in water (Na_2O 4.5%) was added with constant stirring by a motor-driven stirrer to an equal volume of a 10% solution of hydrochloric acid. The liquid set to a gel in five to six hours. It was then broken up, washed with tap water for three days, dried on an air bath at about 80° C., and finally dried to constant volume in an oven at 100° C. This drying process usually required about ten days.

To purify the gel it was refluxed with concentrated nitric acid (s.g. 1.415–1.42) for three days, washed with distilled water until the decanted liquid showed no trace of acid, and dried in an oven at 100° C. The gel thus obtained was colorless, transparent, and very hard. When treated with hydrofluoric acid and sulfuric acid and evaporated no residue was obtained, thus showing the gel to be free of impurities.

Stock carbon tetrachloride was redistilled, the portion boiling at 76.7° C. being used in all adsorption measurements.

Treatment of Gel

Samples of the gel were heated to different temperatures in an electric furnace. The temperature was determined by means of a platinum platinum-rhodium thermocouple. The particular temperature at which each sample was heated was kept constant to within 15° C. at the higher temperatures while

*The substance of this article forms the dissertation of R. I. Rush submitted to the Johns Hopkins University in partial fulfillment of the requirements for the degree of doctor of philosophy.

[1] Patrick and coworkers, The John Hopkins University.

[2] Van Bemmelen: Z. anorg. Chem., **18**, 114 (1898).

[3] E. Berl and W. Urban: Z. angew. Chem., **36**, 57-60 (1923).

the variation was less at the lower temperatures. The gel was maintained at the particular temperature for a period of two hours, and then cooled over calcium chloride in a desiccator.

One sample of the gel was allowed to remain in contact with a .5% solution of sodium sulfate for three days, washed superficially with distilled water three or four times, and dried at 100° C. before being heated at the various temperatures. Analysis showed that this sample of the gel contained .28% of sodium sulfate or one mole of sodium sulphate per one thousand moles of gel.

All samples of the gel used in the adsorption and density measurements were screened to forty mesh.

Description of Apparatus

The furnace used in heating all samples of the gel was an electric furnace of the upright type and contained a platinum-wound core as a heating unit.

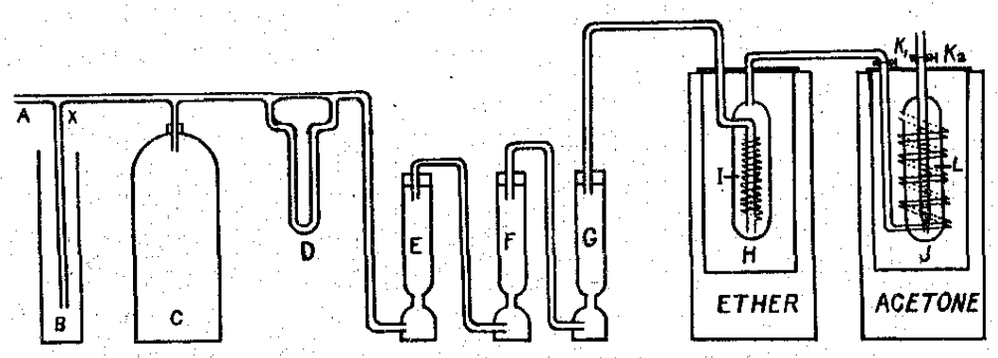


FIG. 1

The temperature was controlled by regulating the amount of current flowing through the furnace by means of a lamp bank. A platinum platinum-rhodium thermocouple with a pyrometer was used to ascertain the temperature. The potential developed by the thermocouple was balanced against that of a standard cell, and the difference was registered in millivolts. The thermocouple was calibrated by subjecting it to the usual fixed temperature points.

The adsorption apparatus consisted essentially of the following:

A cylinder B (Fig. 1) filled with water in which was placed a T tube x. By raising or lowering this tube the rate of flow of the air through the apparatus was regulated. A large bottle C was introduced so that small fluctuations in the air pressure at A would not affect the rate of flow of the air, which was measured by means of the flowmeter D containing water. The tower E containing soda lime, the tower F containing calcium chloride, and the tower G containing phosphorus pentoxide served to purify and dry the the air. The air bath H consisted of a double-walled vessel. In the outer vessel ether was boiled, therby maintaining a constant temperature in the inner vessel in which the bulb I was placed. This bulb was so designed that the air in bubbling through it came in contact with a maximum amount of the liquid carbon tetrachloride contained therein, and thereby became saturated with carbon tetrachloride vapor. The air bath J was of a similar

design but acetone was boiled in the outer vessel. To the outer vessels of H and J reflux condensers were attached. The air containing the carbon tetrachloride vapor to be adsorbed entered the adsorption bulb L contained in this air bath by means of a coil surrounding the bulb, thereby making certain that the vapor was at the same temperature as the gel. The vapor then entered the adsorption bulb L and passed up through the central tube containing the silica gel. Due to the difference in temperature between baths H and J, the air was about 43% saturated with carbon tetrachloride vapor when it passed over the gel.

The adsorption bulb L was of the type used by Patrick and Opdycke.[1] It consisted of a bulb with a central tube in which the gel was placed and a ground glass stopper containing a tube connected with this central tube. The tube by which the vapors entered coiled around the bulb before joining it. The vapors passed through this coil, down through the bulb, and finally up through the gel in the central tube.

The apparatus for determining the density of the gel consisted of a bulb A (Fig. 2) connected by means of a capillary tube C to a side arm graduated in .05 of a cubic centimeter, stopcocks D and E, and an opening at F fitted with a ground glass stopper. The entire apparatus was immersed in a water thermostat in which the temperature variation was ± .02° C., being controlled by an automatic mercury regulator and a heating unit. A motor driven stirrer produced the necessary circulation.

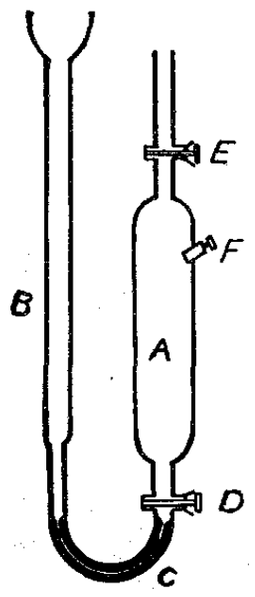


FIG. 2

Experimental Procedure

Adsorption. After the bulb I (Fig. 1) was placed in the bath H and the adsorption bulb L containing the sample of silica gel was placed in the bath J air was allowed to flow through the apparatus for thirty minutes with the adsorption bulb L disconnected. Both the ether and the acetone were allowed to boil. When a constant temperature was reached in the baths H and J the adsorption bulb was connected and the air containing the carbon tetrachloride vapor was allowed to flow through it at the rate of fifteen cubic centimeters per minute. It was necessary to continue this flow for a period of four hours before equilibrium was reached. The bulb containing the gel was weighed before and after the adsorption, and the weight of carbon tetrachloride adsorbed by the gel was calculated from the increase in weight, suitable corrections being made for the free carbon tetrachloride trapped in the adsorption bulb.

Density Determinations. The bulb A (Fig. 2) was evacuated, filled with mercury, and the level of the mercury read on the graduated side-tube B. After the mercury was lowered in the bulb a weighed amount of s ilica ge

[1] Patrick and Opdycke: J. Phys. Chem., **29**, 601-9 (1925).

was introduced, after which the bulb was again evacuated and the mercury allowed to enter. Upon reading the level of the mercury in the graduated side tube B the volume actually occupied by the gel was obtained. From this volume the density was easily calculated. The apparatus was kept in a water thermostat which was maintained at a temperature of 30° C.

Results

The results of this investigation are given in Tables I, II and III. Table I gives the results of the adsorption measurements using pure silica gel. The column headed x/m gives the grams of carbon tetrachloride adsorbed per

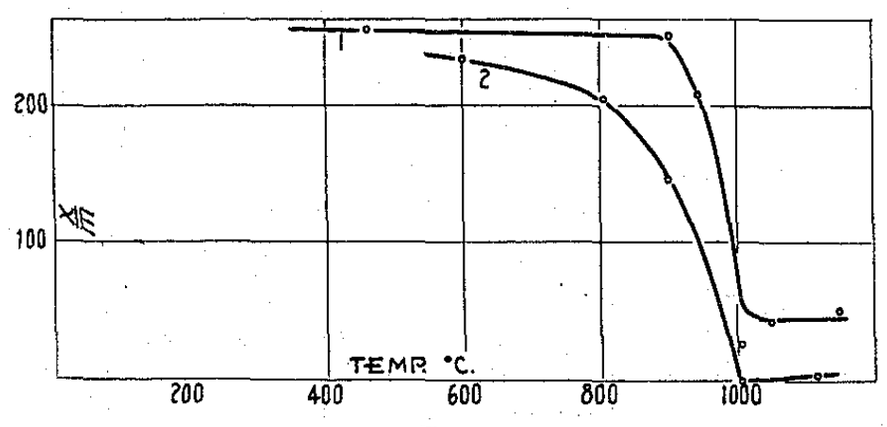


FIG. 3

gram of gel, and the column headed v/m gives the volume in cubic centimeters of the carbon tetrachloride adsorbed per gram of gel. The partial pressure of the carbon tetrachloride and the percent saturation of the air with carbon tetrachloride varied slightly from experiment to experiment, but this variation was not enough to make any appreciable error in the results. The variation was due to the fact that the temperature of the baths H and J varied slightly from day to day with changes in atmospheric pressure.

Curve 1, Fig. 3 shows graphically the results of the adsorption measurements, using pure silica gel. It is to be noted that the adsorption does not change until the gel has been heated above 900° C. Above this temperature it decreases rapidly, reaching a minimum at 1000° C. The fact that it is slightly less at 1000° C. than it is at 1050° C. and 1150° C. is due to the fact that all of the moisture contained in the gel is not driven off until a temperature above 1000° C. is reached.

In Table II are given the results of the adsorption measurements using the gel containing .28% of sodium sulfate or one mole of sodium sulfate per one thousand moles of gel. Curve 2, Fig. 3, shows these results graphically. Here again carbon tetrachloride was used as the vapor to be adsorbed. About the same variations in the partial pressure of the carbon tetrachloride vapor were noted.

In the case of this impure gel the decrease in the adsorption begins at a much lower temperature and is much more gradual. However, it reaches a minimum at 1000° C., as in the case of the pure gel, but in this case the

minimum is zero adsorption. The slight increase above 1000° C. is so slight that it may be properly attributed to experimental error.

The results of the density determinations are given in Table III. The fifth column gives the volume of the capillary space in cubic centimeters per gram of gel calculated from the density, and the last column gives this volume in cubic centimeters per one cubic centimeter of gel. This method of

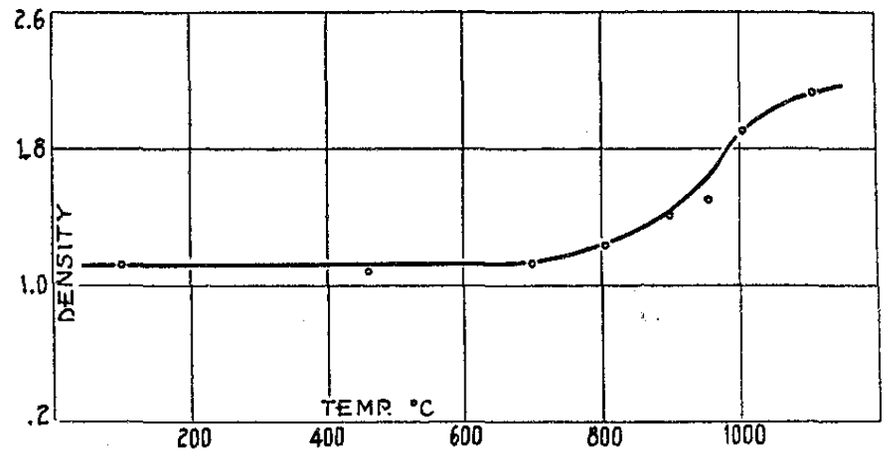


FIG. 4

determining the density of the gel does not give the density of the silica but the density of the gel including the capillary or porous space. The change in density with change in temperature is shown graphically in Fig. 4. Qualitatively these results agree with the results obtained by adsorption, that is, the density increases with the temperature and the adsorption decreases. However, the increase in density starts at a little lower temperature (800° C.) than does the decrease in adsorption (900° C.) and does not reach a maximum until a temperature of 1100° C. is reached.

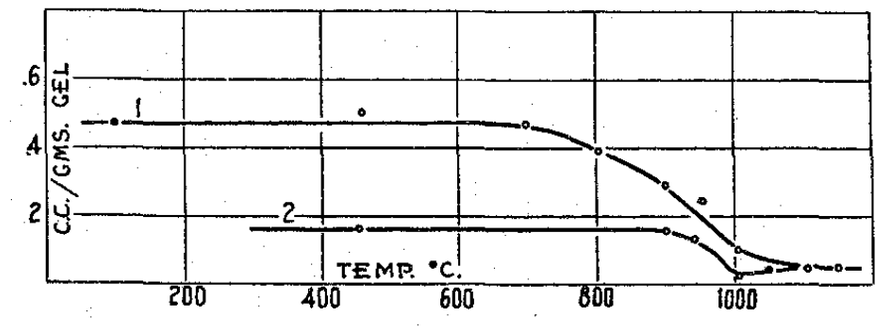


FIG. 5

Curve 1, Fig. 5, shows the volume (cc. per gram of gel) occupied by the capillaries in pure silica gel at various temperatures. This volume was calculated from the density measurements. Curve 2 shows the volume of carbon tetrachloride adsorbed per gram of gel.

TABLE I

Adsorption by Silica Gel

Weight of sample g.	Pre-heating Temp. °C.	Temp. during adsorption °C.	Partial pressure CCl_4 (cm. Hg)	% Sat. of air with CCl_4	x/m g.	V/m cc.
1.2653	470	56.4	17.02	43.0	.2550	.1613
1.7278	900	56.2	17.02	43.3	.2500	.1582
2.0375	945	56.2	17.09	43.4	.2088	.1316
2.6204	1005	55.6	16.75	43.6	.0262	.0164
2.4347	1050	56.5	17.15	43.1	.0426	.0269
2.5927	1150	56.4	17.15	43.3	.0515	.0325

TABLE II

1.8226	600	56.5	17.22	43.3	.2332	.1476
2.0593	805	56.5	17.09	42.9	.2055	.1300
2.2364	900	56.1	17.02	43.5	.1465	.0927
2.5647	950	56.1	16.95	43.3	.0715	.0452
1.9454	1005	56.2	17.09	43.4	.0003	.0000
1.7874	1115	56.3	17.15	43.4	.0038	.0024

TABLE III

Silica Gel—Density

Weight of sample g.	Temp. of Pre-heating °C.	Volume cc.	Density	Capillary Space cc./g. of gel	Capillary Space cc./cc. of gel
1.2835	100	1.14	1.12	.469	.525
1.2537	470	1.16	1.08	.502	.542
1.2479	700	1.11	1.12	.469	.525
1.2617	805	1.02	1.23	.389	.479
1.2469	900	.89	1.40	.290	.407
1.2503	955	.84	1.49	.247	.369
1.2868	1005	.68	1.89	.105	.199
1.2544	1105	.59	2.12	.048	.102
1.2751	1100 (3 days)	.54	2.36	.000	.000

Discussion of Results

Capillary Space. The results of these experiments show that the adsorption ability of pure silica gel is not affected until the gel is heated above 900° C. The density measurements show that some structural changes begin at about 800° C., that is the volume of the capillary space begins to increase at that temperature. Apparently not all of the capillary space is filled with the adsorbed material. However the adsorption measurements were made using comparatively low partial pressures. Patrick and McGavack[1] obtained an

[1] Patrick and McGavack: J. Am. Chem. Soc., 42, 946-78 (1920).

adsorption of .41 cc. per gram gel for sulfur dioxide at 0° C. near the saturation pressure. Patrick and Opdycke[1] obtained an adsorption of .326 cc. per gram of gel for ethyl alcohol at 30° C. near the saturation pressure, and .283 cc. per gram of gel for carbon tetrachloride at 30° C. near the saturation pressure. It appears that in all cases a part of the capillary space is left unoccupied. Considering adsorption as capillary condensation, which it most certainly is to a great extent in the case of silica gel, this may be readily explained. The pores or capillaries in silica gel are generally considered to be conical in shape.[2] It is very probable that the larger ends of these conical capillaries are too large for capillar condensation to take place. Hence the capillary volume calculated from the density determinations described above will always be somewhat greater than that calculated from adsorption measurements. In the density determinations the mercury completely filled all irregularities in the grains of the gel but most certainly did not enter any of the capillary space. The close checks made by successive determinations lend evidence to this fact. All values were checked to within .5%.

W. Bachmann[3] determined the porous space in silica gel by measuring the absorption of water and benzol in the liquid and gas phase. His results vary from .3521 cc. to .6325 cc. per gram of gel. He obtained a number of values between .6160 and .6325 but there seemed to be considerable variation.

Van Bemmelen[4] obtained a value of .71 cc. per cubic centimeter of gel for the capillary space in silica gel. The value obtained from the density determinations in this investigation for gel treated in the ordinary manner and dried at 100° C. was .525 cc. per cubic centimeter of gel. His value for the specific gravity (1.17) compares favorably with that obtained in this investigation (1.12).

The difficulty with determinations of capillary space from adsorption measurements is that we do not know just what happens to the material, as regards its density, when it condenses in the capillaries.

Of course adsorption by silica gel does not depend entirely on the amount of capillary space, but it certainly plays a most important part as is shown by the fact that when we have no capillary space we get practically no adsorption.

Structural Changes. The adsorption measurements seemed to indicate that pure silica gel changes to the crystalline form when heated at 1000° C. or higher for two hours. The density determinations indicated that the gel heated at 1100° C. for two hours might be crystalline, and that the gel heated for three days at that temperature was certainly crystalline. The X-ray diffraction patterns[5] of several samples of the gel are shown in Figs. 6 and 7. In Fig. 6 is shown the diffraction pattern of the pure gel which was heated

[1] Patrick and Opdycke: J. Phys. Chem., **29**, 601-9 (1925).
[2] Patrick and Eberman: J. Phys. Chem., **29**, 220-28 (1925).
[3] W. Bachmann: Z. anorg. Chem., **80**, 202 (1913).
[4] Van Bemmelen: Z. anorg. Chem., **18**, 114-17 (1898).
[5] Thanks are due to L. H. Reyerson and O. E. Harder of the University of Minnesota for making these photographs.

at 700° C. for two hours, along with the diffraction pattern of a high purity crystalline silica sand. It can be seen clearly that this sample of the gel is amorphous, the upper pattern being that of the crystalline silica. Fig. 7 shows the diffraction pattern of the pure gel that was heated at 1100° C. for two hours, along with the sample that was heated at 1100° C. for three days. The former is the upper pattern and the latter the lower pattern. It can be seen that the gel heated at 1100° C. for two hours does not show any diffraction lines. This means that it is not crystalline or at least does not contain enough crystalline material to give a diffraction pattern. The slight line on this pattern is apparently a reflection from the other gel which was exposed along with this sample. The sample of gel heated at 1100° C. for three days

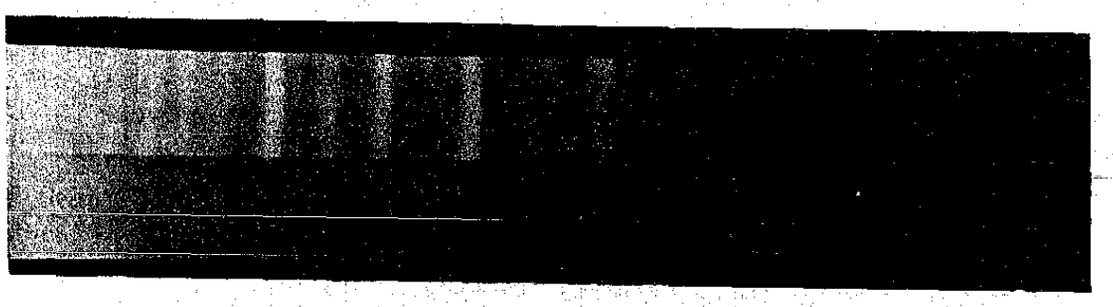


FIG. 6



FIG. 7

(shown in lower pattern, Fig. 7) gave a diffraction pattern which shows clearly that it is crystalline. The interesting fact is that the pattern of this gel does not match that of the pure crystalline silica sand shown in Fig. 6. It is possible that the gel may have contained a small amount of dissolved substance, and that this substance had some influence on the space lattice. In view of the fact that the gel was very pure it is highly probable that a crystalline form of a different structure from that found in the silica sand was obtained.

The fact that the adsorption drops to a minimum in the case of the gel heated at 1000° C. for two hours indicates that at that temperature the capillaries of the gel have closed up, and that what we have is amorphous silica without any appreciable capillary space.

The results of this investigation are not in agreement with van Bemmelen[1] who stated that pure silica gel would retain its structure when heated. These results do not agree entirely with those of Berl and Urban.[2] They stated that pure silica gel would become only partly crystalline when heated at 1000° C.,

[1] Van Bemmelen: Z. anorg. Chem., **18**, 114-17 (1898).

but that if it were boiled with hydrochloric acid before being heated at 1000° C. it would become mostly crystalline. However, they heated the gel for a period of only ten minutes, and it has been shown that longer heating does bring about further changes. The gel used by the author was refluxed with nitric acid in order to purify it. In all probability the gel used by Berl and Urban contained impurities even after the hydrochloric acid treatment, for in the preparation of the gel the hydrochloric acid is the main source of impurities.

Various theories have been advanced to explain the crystallization of amorphous materials when heated.

One theory considers the material as a supercooled liquid. When the molten material cools down, the molecule ceases to be the unit and the atoms arrange themselves into a crystal lattice. According to this theory as the temperature drops below the melting point the rate of crystallization increases to a maximum, remains constant for a certain interval, and then decreases until all of the material is in the crystalline form. In the present investigation the gel was not heated over 1150° C. whereas its melting point is 1600 ° C. to 1750° C. and no such phenomenon as just described was observed.

Another theory states that the gel sinters when heated and that the sintering is accompanied by crystallization. This implies that some of the particles are small enough to melt at a lower temperature than the normal melting point, or that there are some sharp edges that melt below the normal melting point. Hence crystallization may start before the entire mass has melted. The particles of gel used by the author were not small enough to change appreciably the melting point, although some of the edges of the particles may have been sharp enough to have caused such a phenomenon. However, no visible evidence of sintering was obtained.

Still another theory assumes that a minute amount of silica dissolves in the small amount of water present in the gel, and when the material cools this minute amount of dissolved silica forms crystal nuclei around which the rest of the silica crystallizes.

It is known that quartz exists in two forms designated as α quartz and β quartz. α quartz is hexagonal trapezohedral-tetartohedral and is formed at temperatures below 575° C. β quartz is hexagonal trapezohedral-hemihedral and is formed at temperatures between 575° C. and 800° C. Above 800° C. it changes to tridymite which in turn changes to cristobalite at about 1470° C. The crystal angles of α quartz change with increase of temperature up to the inversion point to β quartz (575° C.). Beyond this point they remain nearly constant. At this point there is also a sudden marked lowering of the refractive indices and birefringence. Quartz, tridymite, and cristobalite are usually considered as polymers of a fundamental SiO_2 molecule. Apparently the atoms of α quartz become mobile enough at 575° C. to rearrange to form β quartz, at 800° C. the atoms of β quartz become mobile enough to rearrange to form tridymite, and at 1470° C. the atoms of tridymite become mobile enough to rearrange to form cristobalite.

In the light of these facts it seems highly probable that at 1100° C. the atoms that make up the silica gel aggregate acquire a mobility great enough to allow them to arrange themselves in a crystalline form. Between 700° C. and 800° C. the capillaries begin to close up, but it appears that crystallization does not take place or at least is not complete until a temperature of 1100° C. is reached. The X-ray diffraction pattern (Fig. 7) shows that the gel heated at 1100° C. for three days is crystalline. The assumption that a small amount of silica dissolves in the small amount of water present and thus starts crystallization is in line with the statements made above in regard to the mobility of the atoms. It is perfectly possible that, after the small amount of crystalline silica is formed from the dissolved silica, the atoms of the remaining silica would not arrange themselves in a crystal lattice until a temperature was reached at which they would have the required mobility.

The behavior of the gel containing one mole of sodium sulfate per one thousand moles of gel would indicate that a small amount of sodium silicate is formed and that this material starts the crystallization at a lower temperature. The fact that this gel does not become completely crystalline until a temperature of 1000° C. or 1100° C. is reached would indicate that although crystallization may be started at a lower temperature it is not complete until the atoms have acquired a certain mobility. The melting point of sodium silicate ($Na_2O.2SiO_2$) is 874° C., but it is very probable that in the silica gel its melting point may be considerably lowered. This would account for the fact that in this impure gel crystallization does start much below 874° C.

Summary

1. The adsorption of carbon tetrachloride by silica gel heated at temperatures of 100° to 1150° C. has been studied.

2. The density of silica gel heated at temperatures of 100° C. to 1100° C. has been determined.

3. The effect of impurities on the adsorption of carbon tetrachloride by silica gel has been studied.

4. It has been shown that pure silica gel changes to the crystalline form when heated at 1100° C.

5. A theory has been advanced to explain this structural change.

Chemistry Laboratory,
Johns Hopkins University,
Baltimore, Md.

SOCIÉTÉ DE CHIMIE INDUSTRIELLE
28, Rue St-Dominique
ANNULÉ
PARIS (7e)

COMPRESSIBILITIES OF AQUEOUS SOLUTIONS OF SOME FATTY ACIDS

BY S. VENKATESWARAN

Recently in the course of some experiments on light-scattering acids[1] it was felt that data on the isothermal compressibilities at atmospheric pressure of some fatty acids would be desirable. The present paper describes the results of such measurements carried out in this laboratory for formic, acetic, propionic, and butyric acids. In the direct method of determining the isothermal compressibility of a liquid there is a source of error, first pointed out by Tyrer,[2] which becomes especially serious when the determinations are made with small ranges of pressure as are involved in the present measurements, viz., one to two atmospheres. As the rise of temperature due to compression is extremely small being the order of a hundredth of a degree, the liquid cannot be brought back to its original temperature in any reasonable time. The volume change due to this small rise in temperature being appreciable in comparison with the change of volume due to compression, the error resulting from it may be as high as 10%. Hence following Tyrer, the author has measured the adiabatic compressibilities directly, and from thence calculated the isothermal values.

Experimental

The apparatus consisted of a piezometer made of ordinary soft soda-glass which was enclosed in an outer vessel. The piezometer was attached at one end to a capillary tube provided with a tap and a fine graduated capillary tube open at the end was fused at the other end. After filling with the liquid the piezometer was kept in position inside the outer vessel with a rubber stopper. Sealing wax was used to ensure the joints being completely air tight. This also helped to prevent the rubber stopper from being pushed out on increasing the pressure inside. The piezometer was connected through a side tube in the outer vessel to a manometer and a small compression air pump by means of a stout rubber tubing. The apparatus was essentially of the same pattern as the one used by Tyrer in his earlier experiments with the slight modification that whereas in his apparatus the piezometer was fixed permanently inside the enclosed vesssel, in the present case it was capable of being taken out. This is of advantage in cleaning and filling the piezometer with the liquids for the measurements.

The apparatus was kept in a thermostat and the temperature maintained constant during the course of each series of experiments. The pressures were measured by means of a mercury column in a U tube of sufficiently wide bore to avoid capillary troubles. The differences in pressures were read to one twentieth of a millimetre with the help of a cathetometer and were all reduced

[1] S. Venkateswaran: Ind. J. Phys., **1**, 235, 393 (1927).
[2] Tyrer: J. Chem. Soc., **105**, 2534 (1914).

to standard conditions. Correction was also applied to the small change in pressure caused by the change of level of the liquid in the graduated capillary tube on releasing the pressure inside the apparatus.

It is of the greatest importance to have the liquid in the piezometer absolutely free from entrapped air. The liquids were previously freed from dissolved gases.

The capillary tube was calibrated in the usual way by weighing threads of mercury which filled up a measured length of the tube. One unit division (1 cm) of the capillary tube gave a volume of .001704 cc. The volume of the piezometer was determined by weighing the quantity of water required to fill it at a known temperature. Its volume was found to be 127.10 cc at 23°C. Its volume at other temperatures was calculated by the aid of the known coefficient of expansion of glass.

The proper choice of the lubricant for the tap of the piezometer is a matter of some difficulty, since the usual lubricants are acted on either by water or the organic acids used in the experiments. The difficulty was however overcome by selecting a suitable thick mineral jelly as the lubricant and protecting it from the acids with an intervening column of mercury.

The pressure inside the piezometer was raised to about two atmospheres. After allowing sufficient time for the conditions to become steady, the height of the liquid in the capillary tube was read, as also the height of mercury in the manometer. The pressure was then suddenly released by opening a side tap to the atmosphere and the new position of the liquid column in the capillary tube was noted as quickly as possible. As the whole operation is finished within a fraction of a second the conditions may be said to be truly adiabatic. From the two readings the change in volume was determined, and the pressure change was found from the manometer readings.

The acids used were all Kahlbaum's chemicals. Immediately after the experiment was over, the strength was determined in each case by titrating a known volume of the acid with standard caustic soda solution.

Results

The experimental values of the adiabatic compressibilities of formic, acetic, propionic and butyric acids and their aqueous solutions are given in the following tables. The adiabatic compressibility of water was also determined for comparison with the values obtained by other investigators.

Water

Temperature °C	$\alpha \times 10^6$ per atmosphere
22.6	45.66

(1) 45.49 (Tyrer. Value interpolated, first series of experiments)

(2) 45.73 (Tyrer. Value interpolated. Second series of experiments).

Formic Acid

Strength of acid %	Temperature °C.	$\alpha \times 10^6$ per atmosphere	Strength of acid	Temperature °C.	$\alpha \times 10^6$ per atmosphere
34.70	33.5	43.88	85.19	31.0	50.80
61.51	30.5	44.73	98.80	34.0	57.68

Acetic Acid

Strength of acid %	Temperature °C.	$\alpha \times 10^6$ per atmosphere	Strength of acid	Temperature °C.	$\alpha \times 10^6$ per atmosphere
26.45	35.4	43.69	78.85	27.0	56.66
53.76	33.0	46.68	100.0	26.2	79.86

79.40 (Tyrer. Value interpolated to 26.2° C.).

Propionic Acid

Strength of acid %	Temperature °C.	$\alpha \times 10^6$ per atmosphere	Strength of acid	Temperature °C.	$\alpha \times 10^6$ per atmosphere
49.06	22.4	47.33	76.93	24.4	58.76
56.24	23.4	49.32	100.0	23.6	76.12

Butyric Acid

Strength of acid %	Temperature °C.	$\alpha \times 10^6$ per atmosphere	Strength of acid	Temperature °C.	$\alpha \times 10^6$ per atmosphere
24.00	24.5	48.08	78.05	29.0	64.88
61.76	25.2	59.43	100.0	25.0	80.44

Discussion of Results

1. *Adiabatic compressibility:*—Owing to the compressibility of the glass in which the piezometer is made a small correction is required for the change in volume which it undergoes. The cubical compressibility of glass according to Amagat is 2.2×10^{-6} per atmosphere. Hence if α be the adiabatic compressibility of the liquid, v the observed volume change for a change of pressure of p atmospheres and V the total volume of the liquid

$$\alpha = \frac{v}{Vp} + 2.2 \times 10^{-6}$$

The values for α for water and acetic acid agree closely with Tyrer's values. The adiabatic compressibility of formic acid is lower than that of the other three acids. Aqueous solutions of butyric acid show higher values of α than the other three acids of the same concentration. In all the cases investigated above, the compressibilities of the acid solutions increase slowly with the concentration at the early stages, the increase being much more rapid at higher concentrations.

(ii) *Isothermal compressibility:*—The isothermal compressibility β is connected with the adiabatic compressibility α by the well-known relation

$$\beta = \alpha + \frac{T\left(\frac{dv}{dt}\right)^2}{J.\ v.\ Cp}$$ where

T is the absolute temperature, c_p the specific heat at constant pressure, v the specific volume, and J the mechanical equivalent of heat. In the following tables the values of β calculated by aid of this equation are given for the liquids investigated. The values of v, and cp have been taken from data of other investigators and the values of dv/dt calculated from the specific volume data. For want of available data the values of β for aqueous solutions of propionic and butyric acids could not be calculated.

Water

Temperature °C.	$\alpha \times 10^6$ per atmosphere	Specific volume	$\frac{1}{v} \times \frac{dv}{dt}$	Specific heat	$\beta \times 10^6$ per atmosphere
22.6	45.66	1.0024	.000227	.9982	46.03

(1) 45.72* (Tyrer).

(2) 46.01** (Röntgen and Schneider).

Formic Acid

Strength of acid %	Temperature °C	$\alpha \times 10^6$ per atmosphere	Specific volume[1]	$\frac{1}{v} \times \frac{dv}{dt}$	Specific heat[2]	$\beta \times 10^6$ per atmosphere
34.70	33.5	43.88	.9316	.0006279	.837	47.10
61.51	30.5	44.73	.8814	.0008385	.712	51.06
85.19	31.0	50.80	.8468	.001128	.604	60.09
98.80	34.0	57.68	.8330	.001107	.540	71.62

Acetic Acid

Strength of acid %	Temperature °C	$\alpha \times 10^6$ per atmosphere	Specific volume[1]	$\frac{1}{v} \times \frac{dv}{dt}$	Specific heat[4]	$\beta \times 10^6$ per atmosphere
26.45	35.4	43.69	.9722	.0006029	.902	46.59
53.76	33.0	46.68	.9529	.0008196	.758	52.88
78.85	27.0	56.66	.9409	.0009408	.620	66.40
100.	26.2	79.86	.9590	.001074	.512	95.80

(a) 96.01 (Tyrer)[5].

(b) 98.0 (Drucker)[6].

Propionic Acid

Strength of acid %	Temperature °C	$\alpha \times 10^6$ per atmosphere	Specific volume[7]	$\frac{1}{v} \times \frac{dv}{dt}$	Specific heat[8]	$\beta \times 10^6$ per atmosphere
100.0	23.6	76.12	1.0116	.001102	.548	92.29

* Tyrer: loc. cit. (interpolated for 22°6c from his values at 20° C and 30° C).

** Röntgen and Schneider (Cohen and Schut: "Piezochemie") interpolated for 22°.6 C.

[1] Calculated from Turbaba's values (Landolt-Börnstein Tabellen, (1923)).

[2] Lüdeking (Landolt-Börnstein Tabellen). Determinations were made only at two concentrations. The results given were read from a curve drawn through these and that for water.

[3] Values calculated from Oudemann's results (Landolt-Börnstein Tabellen).

[4] Reis (Landolt-Börnstein Tabellen). Determinations were made at four concentrations. The results given were read from a curve drawn through these points.

[5] Tyrer (loc. cit.). Value interpolated to 26.2°C. from his results at 20°C. and 30°C.

[6] Drucker (Cohen and Schut: "Piezochemie.") Corresponds to 1-300 atmospheres. Obtained by extrapolation.

[7] Zander (Landolt-Börnstein Tabellen).

[8] The value is the mean of the results of Luginin (Ann. Chim. Phys. **27**, 105 (1902)) and Guillot (Landolt-Börnstein Tabellan).

Butyric Acid

Strength of acid %	Temperature	$\alpha \times 10^6$ per atmosphere	Specific volume[1]	$\frac{1}{v} \times \frac{dv}{dt}$	Specific heat[2]	$\beta \times 10^6$ per atmosphere
100.0	25.2	80.44	1.0477	.001065	.526	96.77

In the calculation of the isothermal compressibility of a liquid from its adiabatic compressibility the sources of error lie in the values of dv/dt and cp. However, as the expression involving these quantities, (viz) $\frac{T\left(\frac{dv}{dt}\right)^2}{J.v.cp}$ is a small additive term in the calculation of β these errors have comparatively small effect. In the case of water and acids of lower concentrations this quantity is negligible.

The isothermal compressibility of formic acid is lower than that of the other three acids. Drucker's value for acetic acid when extrapolated to one atmosphere is slightly higher than the present value which as already pointed out agrees very closely with Tyrer's. Therefore, it is not surprising that his values for solutions of the acid are also uniformly higher than the present values.

Summary

The paper gives some experimental results regarding the adiabatic compressibilities of aqueous solutions of formic, acetic, propionic and butyric acids, at a pressure of one to two atmospheres. The isothermal compressibilities are calculated from these results for the acids for which the necessary data are available.

The author desires to express his best thanks to Prof. C. V. Raman, F. R. S., for his constant encouragement and kind interest in the work.

Chemical Laboratory,
Indian Association for the Cultivation of Science,
2108, Bowbazar Street, Calcutta.
July 1, 1927.

[1] The mean of the values of Pierre and Zander (Landolt-Börnstein Tabellen) was taken.
[2] Guillot (Landolt-Börnstein Tabellen).

GERMANIUM. XXII. THE DIHALIDES OF GERMANIUM[1]

BY F. M. BREWER AND L. M. DENNIS[2]

Introduction

In the chemistry of the fourth group of the periodic system very interesting variations in properties and behavior are to be found in those compounds in which the group elements are divalent. This applies particularly to germanium, tin, and lead. The outstanding anomaly of carbon monoxide has long been recognized as a problem whose solution will illuminate the whole field of chemical combination; but the explanation of the change from carbon and silicon, where divalency is so little in evidence, to tin and lead, where it would appear to be in many cases the more natural condition for the element, has probably a far greater fundamental significance. Germanium occupies the intermediate position and the preparation of its compounds in the divalent series is therefore a matter not only of immediate practical interest, for very few of them have hitherto been made, but also of considerable theoretical importance.

Divalency in the case of carbon and silicon appears to be limited to carbon monoxide, a doubtful monoxide of silicon, and the equally questionable existence of the monosulphides. The valency of carbon in the isocyanides raises the larger issue of tautomeric change, which is beyond the scope of this paper. What evidence there is for even the transient existence of a dihalide of carbon comes from the work of Löb.[3] He decomposed the vapor of chloroform by means of a heated wire, and found perchlorethylene to be one of the main products of decomposition. He considered that this was best explained on the assumption that the primary reaction was in accordance with the equation

$$CHCl_3 \longrightarrow CCl_2 + HCl$$

If such a compound does exist, it is subject to immediate polymerization and condensation reactions. Troost and Hautefeuille[4] describe substances which they designate as subfluoride and subchloride of silicon, but the existence of these compounds has not been confirmed.

On the other hand, the dihalides of tin and lead are quite well known, and in the case of lead are distinctly more stable than the corresponding compounds in the tetravalent series. This development of a lower valency, and particularly one which differs by two from the normal group valency, is quite marked in elements of high atomic number, and its theoretical basis has been dis-

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[1] Contribution from the Department of Chemistry, Cornell University.

[2] This article is based upon part of the thesis presented to the Faculty of the Graduate School of Cornell University, by Frederick M. Brewer in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

[3] Z. Electrochem., 7, 907 (1901).

[4] Ann. Chim. Phys., (5), 7, 464 (1876).

cussed by Grimm and Sommerfeld.[1] The fact that the germanium dihalides have been but little investigated is attributable not only to the scarcity of the element itself, but also to the difficulty of isolating and handling what have since proved to be very reactive substances. In the first of his two main articles on germanium Winkler[2] stated that the dichloride is produced by the action of hydrogen chloride upon the metal or upon germanium monosulphide. He described it as a colorless liquid which fumes in the air, but he was really doubtful as to its identity, suggesting the possibility of it being the chloroform, $GeHCl_3$. In his later paper[3] he stated definitely that the product of these reactions was the chloroform, and not the dichloride.

Winkler made the tetrabromide and tetra-iodide of germanium but he does not recount any attempt to prepare the lower halides. In the case of the fluoride, he found evidence of the formation of a difluoride in the reaction of hydrogen upon potassium fluogermanate. Actually his experiment denotes a reduced complex rather than a free difluoride.

In preparing germanium tetra-iodide by the action of iodine vapor upon heated germanium Dennis and Hance[4] obtained a small yield of a substance which proved to be germanous iodide. It appeared in the form of yellow hexagonal crystals and was comparatively stable in air. They made no further investigation of the compound. Dennis, Orndorff, and Tabern[5] prepared germanium chloroform by passing hydrogen chloride over the product that resulted when the vapor of germanium tetrachloride was passed over metallic germanium at high temperature. This product was presumably germanium dichloride. It was rapidly attacked by moisture and by the oxygen of the air. The study of this substance was not completed at that time.

The general methods which suggested themselves for the preparation of the dihalides were:—

(1) The restricted action of halogens upon metallic germanium, (2) The reduction of the tetrahalides, (3) The dissociation of the tetrahalides, (4) The removal of the hydrogen halide from compounds of the chloroform type, and (5) Metathetical reactions.

Experimental

Attempts to prepare Germanium Dichloride.

(a) *Metathetical Reactions.*

Metallic germanium was prepared by the method of Dennis, Tressler and Hance.[6]

A small quantity of the finely divided germanium was heated with mercuric chloride in an inclined tube of hard glass in an atmosphere of nitrogen,

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[1] Z. Physik, **36**, 36 (1926).
[2] J. prakt. Chem., **142**, 177 (1886).
[3] J. prakt. Chem., **144**, 177 (1887).
[4] J. Am. Chem. Soc., **44**, 2854 (1922).
[5] Dennis, Orndorff and Tabern: J. Phys. Chem., **30**, 1049 (1926).
[6] J. Am. Chem. Soc., **45**, 2033 (1923).

at a pressure of 15 mm. There was no evidence of the formation of germanium dichloride. When mercurous chloride was used, germanium tetrachloride formed and condensed on the walls of the tube. On further heating, mercury distilled up the tube, and where it condensed with the tetrachloride a yellow product was formed. The experiment indicated that a reduction of germanium tetrachloride by mercury takes place, but separation of the products would be difficult.

(b) *Reduction of Germanium Tetrachloride.*

Instead of mercury, a ½% sodium amalgam was used as the reducing agent, the reaction being carried out in an atmosphere of nitrogen. A dark powder began to form in the cold upon the surface of the amalgam, and increased in amount on the application of heat. The final product was a black powder mixed with mercury and the residual amalgam. The powder appeared to be metallic germanium. Dilution of the tetrachloride with toluene did not affect the result. Similar products were also obtained with the use of aluminum amalgam at elevated temperature.

Tin foil and tin amalgam had no effect upon the tetrachloride at its boiling point, nor was there any indication of reaction upon passing the vapor of the tetrachloride over heated tin amalgam. Magnesium ribbon, neither by itself nor in the presence of mercury, appeared to effect reduction when refluxed with germanium tetrachloride, nor was zinc dust any more effective. When germanium tetrachloride was refluxed with freshly cut sodium, a black coating formed on the surface of the metal.

The action of metallic silver was next studied. Crystalline silver, made by direct electrolysis of a solution of silver nitrate, had no effect when refluxed with the tetrachloride, but a vigorous reaction occurred when the vapor of germanium tetrachloride was passed over the heated crystals. There was some indication that silver chloride had been formed in the reaction, but germanium dichloride was not found among the products of the reaction.

Gomberg's[1] "molecular silver" was then used. This gives a very fine product of higher reducing power and catalytic activity. Nevertheless, it appeared to have no effect upon germanium tetrachloride, nor did it catalyze its reduction by organic reducing agents.

The statement of Dennis and Hance[2] that germanium tetrachloride dissolves in acetone with the formation of a light orange-colored liquid made it appear possible that the acetone reduced the tetrachloride. It was found, however, that germanium tetrachloride could be refluxed with acetone for three days without any development of color. As the reduction may have been due to the presence of aldehyde in the acetone originally used, paraldehyde was added to the solution, which was again refluxed. The mixture eventually became pale yellow in color, but no solid could be isolated. Formaldehyde bubbled through liquid germanium tetrachloride at room temperature or at the boiling point of the tetrachloride was equally ineffective as a reducing agent.

[1] Ber., 39, 3287 (1906).
[2] J. Am. Chem. Soc., 44, 307 (1922).

(c) *Reactions with Germanium Chloroform.*

There remained the possibility of preparing the dichloride from the chloroform. Laubengayer[1] had shown that hydrogen chloride reacts with metallic germanium to give a mixture of germanium chloroform and germanium tetrachloride which cannot be resolved into its components by fractionation. This mixture forms, nevertheless, by far the most convenient source of germanium chloroform.

The two methods available for the preparation of the dichloride from the chloroform were thermal dissociation or purely chemical reactions. Experiments upon the thermal decomposition of the chloroform present the same difficulties as the reduction of germanium tetrachloride by germanium. If whatever dichloride that may be formed remains in the heated region where dissociation of the chloroform takes place, the dichloride is immediately decomposed into germanium and germanium tetrachloride. This was demonstrated by a repetition of Löb's experiment with chloroform vapor, using a rather simpler apparatus. A coil of fine platinum wire was sealed into a glass tube about one centimeter in diameter, which had a bulb attached at either end. The chloroform-tetrachloride mixture was brought into one of these bulbs, and was made to pass slowly over the platinum by regulated cooling of the other bulb. The platinum was heated electrically, and at a temperature just below red heat, first a few drops of liquid, and then a thin film of cream-colored solid, were deposited on the walls of the tube. As the temperature of the wire was raised, the solid dissociated and germanium and germanium tetrachloride were formed.

It was then sought to remove the elements of hydrogen chloride from germanium chloroform or from a mixture of the chloroform and the tetrachloride, in the hope that germanium dichloride or a mixture of the di- and tetra-chlorides would result. The tetrachloride could then be separated by distillation. Moreover, if the agent that effected the removal of hydrogen chloride should form with it a volatile compound, or even by its presence alter the equilibrium

$$GeHCl_3 \rightleftarrows GeCl_2 + HCl$$

it should be possible to obtain solid germanium dichloride in a pure state.

The simplest compounds which fulfill this function are the unsaturated hydrocarbons, for they should be able to take up the elements of hydrogen chloride to give the chloro-substituted paraffins, which are comparatively volatile. A slight distillation should then suffice to separate the dichloride from the reaction mixture. Toward the close of this investigation it was found that ethylene could thus be used for the preparation of germanium dibromide, and the application of this reaction to the synthesis of the dichloride is now being studied.

Another class of compounds which might be employed for the removal of hydrogen chloride are the substituted ammonia derivatives, but these are

[1] Dennis, Orndorff and Tabern: loc. cit.

polar compounds and are as a rule insoluble in organic solvents; consequently success in effecting a satisfactory separation in this manner seemed remote.

It was possible, however, that oxonium derivatives might serve the purpose. Ether takes up hydrogen chloride at low temperatures to form a definite hydrochloride and although this dissociates upon warming, it was hoped that by fractionation under extremely reduced pressure, there would not be sufficient dissociation to regenerate germanium chloroform. The reaction of ether upon a mixture of germanium chloroform and germanium tetrachloride proved to be more complicated than was expected. A mixture of the three substances was placed in a bulb which was joined to a receiver that could be cooled in liquid air. The contents of the bulb first separated into two liquid layers, both of which were colorless. Of these the upper was the more volatile, the lower developing a pale yellow tint during the gradual disappearance of the upper. When warmed to 50°, the liquid became viscous, and changed in color from yellow to orange. Finally, on raising the temperature to 90°, a bright yellow solid was deposited and the liquid phase disappeared entirely.

Analyses were carried out at various stages of the distillation, but consistent results could not be obtained in successive experiments. The final product always yielded a much smaller percentage of chlorine than germanium dichloride would contain, and it seemed evident that treatment with ether not only breaks down the germanium chloroform, but that the reaction continues at the expense of the dichloride.

Further study of the preparation of germanium dichloride was deferred for the time being.

Germanium Dibromide.

As Dennis and Hance[1] had succeeded in preparing a stable specimen of germanium di-iodide, it was thought that the dibromide might more easily be obtained than the dichloride, and that at the same time an investigation of its properties might indicate a technique for the isolation of the dichloride. It was to be expected that the action of hydrogen bromide upon germanium would resemble that of hydrogen chloride, in which case a mixture of germanium bromoform and germanium tetrabromide would result, although there was always the possibility that by careful temperature control the dibromide might be produced in a pure state.

Hydrogen bromide was prepared by the method of Recoura,[2] the bromine, however, being covered with concentrated hydrobromic acid instead of with water. The gas, dried by passage through U-tubes containing fused calcium bromide, was led over germanium contained in porcelain boats in a hard glass tube which could be heated in an electric furnace. The reaction tube was connected with a U-tube receiver similar to that described by Dennis and Hance[3] for their preparation of germanium tetrachloride. To avoid any oxidation of the product, the apparatus was filled with hydrogen bromide before heating was begun. Condensation of the product was effected by ice and salt.

[1] J. Amer. Chem. Soc., **44**, 2854 (1922).
[2] Compt. rend., **110**, 784 (1890).
[3] J. Am. Chem. Soc., **44**, 304 (1922).

Appreciable reaction began at about 400°. The run was concluded at a somewhat higher temperature. The reaction proceeded slowly at the beginning, but a good yield was eventually obtained. As in the similar experiment with hydrogen chloride, if the passage of gas was slow, a certain amount of yellow solid, presumably the dibromide, was deposited in the forward end of the tube, but this could be completely removed as a volatile liquid by the action of more hydrogen bromide.

The liquid product was colorless, but when air was admitted to the reaction tube after the conclusion of the experiment, the few remaining drops of liquid in it were converted to a sticky, yellow solid. A vacuum distillation apparatus[1] was then prepared for the fractionation of the liquid condensed in the receiver. In the first distillation, the pressure maintained in the system was not carried below 4.5 mm. and this was sufficient to distill only a portion of the main product into the vacuum system. The residue was reserved for further fractionation at lower pressures. While the distillation was in progress two layers separated out in the receiver bulb. One of these became distinctly yellow. The fraction which distilled over evidently contained a large amount of free hydrogen bromide, since its zero vapor pressure was 157.5 mm. This was considerably higher than the vapor pressures of either the chloroform or tetrachloride, and therefore could hardly be expected to come from any of the bromine compounds of germanium, which should be even less volatile. The hydrogen bromide was therefore distilled off before the main fractionation was attempted.

When one of the valves was opened, however, and liquid air was applied to a condensing bulb connected with it, only a minute quantity of liquid was found to have condensed in the bulb, while a cream-colored solid was deposited throughout the connecting parts of the apparatus. When the condensate in the bulb was again allowed to evaporate, it completely removed all of this deposit. From this it appeared that in the absence of an excess of hydrogen bromide, the germanium bromoform is dissociated into the dibromide and hydrogen bromide, and that the effect of the liquid air is to condense some of the more rapidly diffusing hydrogen bromide, thus disturbing the equilibrium and eventually depositing the dibromide. This was confirmed by later work. It also became clear from this experiment that fractionation in the vacuum apparatus was not feasible, because it was impossible to keep the valves free from the deposit.

The residue left from the first attempted fractionation of the mixture produced by the action of hydrogen bromide on germanium was kept for several days in a vessel sealed from the air, and at the end of that period was observed to have deposited a few long, pale yellow crystals. As these did not melt below 100°, even though moist with residual mother liquor, they could not be crystals of germanium tetrabromide. Since it had been shown that fractionation tended to condense hydrogen bromide, and therefore presumably

[1] Laubengayer and Corey: J. Phys. Chem., 30, 1043 (1926).

leave behind germanium dibromide, it seemed probable that these might actually be crystals of the desired compound.

Some of them were eventually extracted from the receiver in which they had been held, and were washed rapidly with benzene and dried. They became sticky on exposure to the air, and on this account it was impossible to obtain the exact weight of a sample, but the ratio of germanium to bromine was determined. All analyses in connection with the dibromide were made by dissolving the sample, with or without the aid of hydrogen peroxide, making up the solution in a graduated flask to a known volume, determining bromine as silver bromide gravimetrically in one portion, and germanium by the method of Dennis and Johnson[1] in another. The atomic ratio of germanium to bromine in this preparation was 1:1.93.

The results of this analysis and the behavior of the crystals justified an attempt to prepare germanium dibromide by the continued fractionation of the mixture which contained presumably germanium bromoform and tetrabromide. The liquid was first subjected to pumping at ordinary temperatures. Later the temperature was raised to 90°. There formed a thin upper layer of yellow color which deepened in intensity with further pumping. The lower layer was colorless. As evaporation proceeded, the colorless layer disappeared and, on cooling, crystals were deposited from the yellow solution. The germanium tetrabromide was then pumped out, leaving a cream-colored crystalline deposit. Analysis of this product showed the ratio Ge:Br = 1:2.04. A second preparation by this method gave the ratio 1:2.06. Although the samples were not pure, the analytical results left no doubt that the solid product was chiefly germanium dibromide.

Attempts to fractionate the product by heating in an oil bath at 125° to 130° under reduced pressure were unsuccessful. The greater part of the substance melted and began to decompose, setting on cooling to a yellowish brown mass which became pasty on exposure to the air. It dissolved completely in acetone, but not to any appreciable extent in benzene.

The preparation of the dibromide was next attempted by the action of zinc upon the mixture of germanium bromoform and germanium tetrabromide. Pure zinc was prepared by the electrolysis of a solution of zinc sulphate between a zinc anode and a copper cathode. It was then added to a solution of the bromoform—tetrabromide mixture in benzene. There was a vigorous reaction on warming, resulting in a yellow solution which turned cloudy on cooling because of the separation of an oil. The liquid showed remarkably strong reducing power. On repetition of the experiment without benzene, almost colorless crystals were deposited. These behaved like the dibromide hitherto prepared.

An apparatus for the application of the zinc reaction was then constructed (Fig. 1). This consists of a reservoir *A* for the liquid mixture, to which is joined adapter *B* from the generating tube. On the other side, *A* has an outlet tube *C* which is fused into a wide slip-joint *D*. *E* is the reaction vessel

[1] J. Am. Chem. Soc., **47**, 790 (1925).

and in this is placed a small quantity of zinc. It has a side tube F to which is connected by a normal slip-joint, G, the manifold receiver H. This has its own side-tube with stop-cock for attachment to the vacuum system. The side-tube F of the reaction chamber is plugged prior to the experiment just in front of the stop-cock. The plug originally used was a mixture of asbestos fibre and glass wool, but pure cotton was eventually substituted. Its function is to retain the zinc crystals and insoluble products of the reaction.

In the first experiment with this apparatus, a sample of the bromoform-tetrabromide mixture was run upon the zinc in presence of air, and was then frozen while the air was pumped out of the system. The zinc was warmed, and gas was liberated. This was removed by cautiously opening the stop-

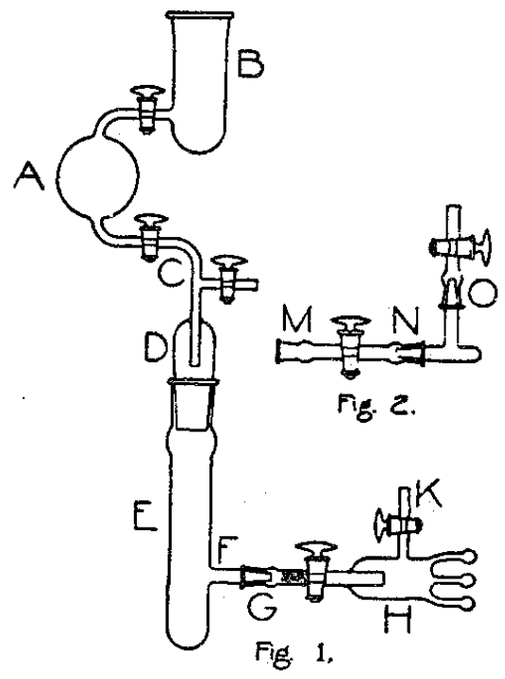


Fig. 2.

Fig. 1.

cock connecting the reaction vessel with the vacuum system from time to time. When the reaction had subsided, the apparatus was turned through 90°, so that the hot solution could run through the plug and stop-cock into the receiver H.

The cloudy yellow suspension noticed in the reaction vessel gave a clear, greenish yellow filtrate. A much larger quantity of solid separated from the solution than had been the case in the thermal decomposition experiments, and it was distinctly crystalline in form. In appearance and in behavior on fractionation, the yellow liquid closely resembled that obtained by the former method. The tetrabromide, which was removed by pumping, was in this case almost entirely free from bromoform, as was shown by its solidification at room temperature, and the lack of any colored products on hydrolysis. Qualitative analysis of the residue showed that it was free from zinc. The zinc which had been used in the reduction became coated with a black powder, which was apparently metallic germanium.

Preliminary experiments revealed difficulties in sampling and analytical procedure, and the apparatus was therefore modified by the introduction of

interchangeable slip-joints, but the principle of the method remained the same. Instead of a manifold receiver, the new receiver consisted of a single tube consisting of two slip-joints at right angles, as shown in Fig. 2. The slip-joints made it possible to clean the apparatus and quickly re-assemble it. Two caps were made from portions of the slip-joints, and these were placed upon the sample tube after it had been detached from the apparatus. Analysis of the preparations made in this apparatus showed that if the dibromide is formed in crystals of appreciable size, it is extremely difficult to remove the tetrabromide which is occluded by them: the product contained only germanium and bromine, but the bromine was always in excess of that required for germanium dibromide. Attempts to remove the tetrabromide by prolonged heating at 90° under reduced pressure caused some decomposition of the dibromide. Attempts to wash it out with benzene or toluene removed both dibromide and tetrabromide without appreciably altering the ratio of germanium to bromine, and always left the sample contaminated with the solvent. For these reasons the tetrabromide was removed by rapid distillation, with consequent formation of small crystals which were then heated to 90° for a short time, and then pumped for a long period at 30°. For analysis, the minimum quantity of absolute alcohol was used for their solution, and great care taken to extract all of the germanium from the sulphide precipitate by the repeated application of ammonium hydroxide.

Analysis:— Substance, 0.3286. Wt. of GeO_2, 0.1450 = 0.1006 Ge. Wt. AgBr = 0.5304 = 0.2257 Br. Calculated Ge, 31.23 per cent., Br, 68.87 per cent. Found Ge, 30.61 per cent., Br, 68.69 per cent. Weight ratio Ge: Br = 1:2.24. Atomic ratio = 1:2.04.

The results show that while the determination of bromine in the product was accurate, there was loss of 2 mg. of germanium in the analysis. The data suffice, however, to establish the identity of the compound.

Properties of Germanium Dibromide.—Prepared in the manner described above, germanium dibromide is a colorless, crystalline solid. If the crystallization is rapid, the crystals appear as very small, glistening plates; more gradual crystallization results in the formation of needles.

When heated, the substance behaved like the product obtained by the thermal decomposition of the bromoform. It left a black residue and simultaneously there were formed drops of an oily liquid which afterwards volatilized. The full decomposition is probably represented by the equation—

$$2\ GeBr_2 = Ge + GeBr_4$$

The compound was not appreciably soluble in hydro-carbons (benzene, toluene) unless germanium tetrabromide was also present. It dissolved in alcohol and acetone to give colorless solutions of strong reducing power. The solution in acetone decolorized bromine water far more rapidly than the acetone itself. Water hydrolyzed the compound to the yellow hydrated germanous hydroxide, but an excess of water dissolved the product to give a solution showing all the characteristics of the germanous ion.

Germanium dibromide absorbs bromine but the reaction is not vigorous. Heat is developed and the resulting product is germanium tetrabromide. Germanium dibromide unites with hydrogen bromide to form the bromoform. (See below).

It is interesting to note that the solution of the dibromide in the tetrabromide is always yellow, whereas in the solid state both are colorless. If, as is probable, the color of the solution is due to the unsaturated nature of the dihalide, it must be assumed that the compound in the solid state is polymerized. This would not only bear out a relation to carbon which can form only the polymerized tetrachlorethylene in place of the dichlormethylene, but would also resemble the behavior of the definitely unsaturated carbon compounds, the triphenylmethyl series. These compounds develop a really intense color only in solution, in which they have been shown to have the dissociated, or unsaturated, constitution.

Germanium Bromoform.

Hydrogen bromide was passed over a sample of germanium dibromide prepared in the vacuum apparatus, which for this experiment was equipped with a reservoir bulb for the gas. The chain was filled with hydrogen bromide at room temperature and atmospheric pressure. The gas was first condensed on the dibromide by means of solid carbon dioxide, but the union of the gas with the dibromide, except when the latter had been deposited in a very thin layer, was rather slow. The rate of reaction increased considerably on warming to 40°. A liquid, which was at first rather cloudy but which cleared on standing in contact with hydrogen bromide, was formed in the receiver. By analogy to the chloroform it was expected that this liquid would prove to be the corresponding germanium bromoform.

An attempt was made to distill this product into a weighed tube fitted with a stop-cock and slip-joint for attachment to the vacuum chain. During distillation at 90°, however, the distillate was observed to decompose throughout the system and to give a white deposit just as in the original fractionation carried out in the vacuum apparatus. When more hydrogen bromide was introduced from the reservoir, this white deposit disappeared and a liquid collected in the sample tube. This liquid remained clear at 0° even when the pressure was reduced to 1.9 mm. which was the value obtained for the 0° vapor pressure of the compound. When the temperature rose to 10° the pressure was 2 mm. and the liquid was no longer clear. This cloudiness did not disappear when hydrogen bromide was admitted to the liquid at 10° but the turbidity vanished when the sample was warmed. When this clear product was heated to 80° the liquid again became turbid probably because of incipient thermal dissociation. Because of the extremely slow absorption of hydrogen bromide by the liquid, except over a very small range of temperature, it was impossible to obtain definite information concerning the equilibrium pressures by starting with the dissociation products.

Analysis:—Since dissociation of the liquid was negligible at 0° or lower temperatures, the sample was held at −10° and the apparatus was evacuated

with a pump to remove any dissolved hydrogen bromide. The sample tube was then closed and was detached and weighed. If dissociation occurred when the sample tube came to room temperature, any evolved hydrogen bromide remained in the closed tube and the dissociation therefore did not vitiate the analytical results.

Substance, 0.4015. Calcd. for $GeHBr_3$: Ge, 0.0930 = 23.16 per cent.; H, 0.0014 = 0.23 per cent; Br. 0.3071 = 76.51 per cent. Found: Ge, 0.0933 = 23.23 per cent; Br, 0.3068 = 76.41 per cent; H, by diff. = 0.36 per cent.

The above analysis identifies the liquid as germanium bromoform, and its production in this manner is evidence that the solid from which it was made was germanium dibromide.

Melting Point:—Before the analysis was made, the sample tube was cooled to $-60°$ and its contents was thus solidified. The melting point was found to lie between $-25°$ and $-24°$. A second sample melted at $-24°$.

It was observed that when bromine is passed through the liquid product that results from the action of hydrogen bromide on germanium, a considerable amount of hydrogen bromide is evolved and there is formed a homogenous product showing the physical constants and chemical behavior of germanium tetrabromide. This shows conclusively that when hydrogen bromide acts upon germanium, a mixture of germanium tetrabromide and germanium bromoform results.

Germanium Di-iodide.

Dennis and Hance[1] found that germanium di-iodide was formed as a product of the reaction between germanium and iodine and also by the dissociation of germanium tetra-iodide at temperatures above 440°. They described it as a yellow solid crystallizing in plates and belonging to the hexagonal system. Their experiments indicated that it should prove a fairly simple matter either to effect dissociation of the tetra-iodide at high temperatures or to displace the equilibrium, $GeI_4 \rightleftarrows GeI_2 + 2\ I$, towards the right.

The action of germanium tetra-iodide upon germanium heated to various temperatures between 370° and 600° gave a small yield of germanium di-iodide immediately in the neighborhood of the metal. Hydrogen iodide, acting upon germanium below 400°, gave germanium tetra-iodide as a finely divided, bright-yellow powder. On raising the temperature of the reaction tube, the hydrogen iodide dissociated and the subsequent course of the reaction was essentially that of free iodine upon the metal. Both hydrogen and acetylene reduced germanium tetra-iodide to some extent, but most of the tetra-iodide volatilized before reduction had taken place. In addition to the volatilization of the tetra-iodide at low temperatures, all of these methods were unsatisfactory because of the equilibrium which exists between the two iodides and free iodine at the higher temperatures where the reaction velocity is appreciable.

[1] J. Am. Chem. Soc., **44**, 2854 (1922).

Anhydrous stannous chloride and mercurous chloride reduce germanium tetra-iodide, but the final reaction product consists of mixtures of the tetra-chloride, tetra-iodide and di-iodide of germanium together with stannic halides and mercuric halides respectively. In the latter case, metallic germanium was also formed.

It was found that the germanium di-iodide which had been prepared in small quantity by the action of iodine vapor upon germanium was only slowly hydrolyzed by cold water. It therefore seemed probable that it would be stable in concentrated hydriodic acid, and consequently might be prepared by solution of hydrated germanium monoxide in that acid.

A mixture of the hydrated monoxide and dioxide of germanium was prepared by adding ammonium hydroxide to the chloroform-tetrachloride mixture, and carefully heating the product. The hydrated oxides were dissolved in concentrated hydriodic acid and the tetra-iodide, which is only sparingly soluble in the concentrated acid, was separated from the solution by filtration. The filtrate, when cooled, deposited a large quantity of feathery, yellow crystals which did not resemble in any way the di-iodide previously prepared. Examination of this substance indicated that it was impure germanium iodoform.

To avoid the formation of the iodoform, an excess of the mixture of the two hydrated oxides was caused to act upon concentrated hydriodic acid, the temperature being kept below 40°. The contents of the flask was then heated to 60° and was filtered. The clear, yellow filtrate deposited well-formed hexagonal plates which were washed with benzene to remove germanium tetra-iodide.

Analysis:—Calcd. for GeI_2: Ge = 22.24 per cent.; I = 77.76 per cent. Subst., 0.4082, 0.3856. Found, GeO_2, 0.1300 = Ge, 22.11 per cent; GeO_2, 0.1239 = Ge, 22.30 per cent. Subst. 0.4074, 0.5705. Found, I, 0.3144 = 77.37 per cent; 0.4417 = 77.42 per cent.

Properties:—Germanium di-iodide is a yellow solid which crystallographically is very similar to lead iodide. It is insoluble in hydrocarbons, but appears to dissolve slightly in chloroform and carbon tetrachloride. It is soluble in concentrated hydriodic acid and can be recrystallized from this medium, except when both acid and di-iodide are present in high concentration. It is soluble in dilute acids and in water, the solutions having the reducing properties associated with the germanous ion. When exposed to the air, the di-iodide is slowly hydrolyzed and germanium dioxide is formed. When preserved in a sealed tube the substance is quite stable. When heated in the air, it does not melt, but at 210° is rapidly oxidized to a mixture of germanium dioxide and tetra-iodide. A sample was placed in a capillary tube which was evacuated and then sealed. When the tube was heated to 240°, a yellow sublimate filled the capillary, and at 265° sublimation was rapid. The color of the solid changed meanwhile from yellow to red. This shows that, at higher temperatures, the di-iodide breaks down, forming germanium and germanium tetra-iodide.

Summary

The preparation of germanium dibromide, germanium bromoform, and germanium di-iodide are described, together with attempts to prepare pure germanium dichloride. It is shown that the dihalides of germanium possess strong reducing power similar to the dihalides of tin, and that the germanium bromoform, and probably also the iodoform, are produced by the action of the halogen acid upon the corresponding dihalide of germanium.

Ithaca, New York.

19 -137

A LABORATORY STUDY OF NITROGEN FIXATION BY THE HIGH TENSION ARC

BY PHILIP G. COLIN[1] AND HERMAN V. TARTAR

Introduction

In previous work from this laboratory,[2] results have been reported on the influence of reduced pressure on the yield of fixed nitrogen from the high tension electric arc. The data were secured under conditions in which the velocity of the molecules of gas through the arc increased as the pressure was reduced. Results were also presented dealing with the equilibrium: $N_2 + O_2 = 2\ NO$; equilibrium being secured by passing the gases repeatedly through the arc at atmospheric pressure.

This investigation deals with (1) the effect of reduced pressure on the yield of fixed nitrogen with a constant velocity of the molecules of gas through the arc and (2) equilibria obtained in an arc with variation of conditions, such as pressure and composition of the initial gas.

Historical

The oxidation of nitrogen in an electric arc is a long known process and the literature has become quite voluminous. An extensive review will not be given. It will suffice to discuss briefly only that literature which has a direct relation to the experimental results presented herein.

(a) Effect of Pressure.

The investigations on the effect of pressure on the oxidation of nitrogen by means of the electric arc are not numerous. Haber and Holwech[3] used a small arc furnace of the Schönherr type for the study of the formation of nitric oxide in the high tension arc under pressure. The current was varied from 0.55 to 1.5 amperes, the power from 660 to 1650 watts and the gas flow from 2940 to 8700 liters per hour. The most favorable yield was 76 grams of nitric acid per kilowatt-hour at a pressure of two atmospheres, although the volume concentration was only 0.36 per cent.

Haber and his co-workers,[4] using an alternating current with small vertical arcs between electrodes of platinum, oxidized iron and Nernst filaments under a pressure of 100-150 mm. and with a slow circulation of gas (mixtures of N_2 and O_2) succeeded in obtaining a percentage by volume of 9.8%NO for air, with a current of 0.24 ampere at 5000 volts in the case of iron electrodes and 0.35 ampere at 3700 volts in the case of Nernst glower electrodes. For mixtures of equal volumes of N_2 and O_2 a yield of 14.4% and for mixtures of 81.7

[1] Du Pont Fellow in Chemistry at University of Washington 1924-1926.

[2] Tartar and Perkins: J. Phys. Chem., 30, 595-616 (1926).

[3] Haber and Holwech: Z. Elektrochem., 16, 810 (1910).

[4] Haber and Koenig: Z. Elektrochem., 13, 725 (1907); 14, 689 (1908); Haber, Koenig and Platou: 16, 789; Haber and Platou: 796 (1910).

parts O_2 and 18.3 parts of nitrogen 12.1% NO was obtained. The most efficient gas pressure was about 100 millimeters of mercury. With a direct current arc burning in a quartz tube a maximum concentration of 8.16% NO (by volume) was obtained at a pressure of 150 millimeters of mercury, with a current of 0.27 ampere at 1400 volts and with a gas velocity of 6 liters per second.

Morden[1] reports results showing a yield of approximately 90 grams of nitric acid per kilowatt-hour (concentration 1.5 to 2.5% NO by volume) at a pressure of 590 mm. of mercury. This was accomplished with a short direct current arc between a water cooled silver anode and an iridium cathode coated with calcium oxide: current 0.115 ampere at 240 volts, air velocity 43.7 liters per hour. The cathode was heated with a secondary current to stabilize the arc. Morden claims that heating the cathode does not affect the yield. Holwech[2] was able to practically duplicate Morden's results. Holwech and Koenig[3] continued the work with short, direct current arcs and secured a yield of 84 grams of nitric acid per kilowatt hour (concentration 2.3% NO by volume) at 500 mm. pressure, using an iron cathode and water cooled copper anode with a current of 0.2 ampere at 280 volts. The gases from the arc were drawn off through a water cooled capillary. Heating the cathode with a secondary current was found to be unnecessary. Attempts to use more energy in the arc gave smaller yields. Reversing the current and also using an alternating current were less successful.

Haber and Holwech[4] tried the use of a direct current arc at pressures greater than atmospheric. The arc was provided with a water cooled copper cathode and iron anode: the air was brought in tangentially at the bottom of the furnace in order to give a whirling motion to the arc. Currents varying from 0.55 to 1.5 amperes at 700 to 2075 volts were used with pressures varying from 2 to 21 atmospheres. The best yield was 76 grams of nitric acid (concentration 0.36% NO) per kilowatt hour at a pressure of 2 atmospheres. Increase of pressure was not found to be beneficial to yield.

Briner and Naville[5] made a study of the effect of pressure on the yield from alternating current arcs between wires of different metals (Fe, Ni, Pt, Ir, Zn) and employed various mixtures of nitrogen and oxygen. They found the yield to depend upon the nature of the electrode but that in each case a maximum yield was obtained using an excess of nitrogen at 700 mm. and 100 mm. pressure and a minimum at 500 mm. The yields were low, not greater than 20 grams of nitric acid per kilowatt hour.

The Nitrogen Products Committee (British)[6] state that "recent experimental work in Switzerland has shown that the yield of combined nitrogen from arc furnaces can be increased by more than 25 per cent by the addition

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[1] Morden: Trans. Am. Electrochem. Soc., **14**, 133 (1908).
[2] Holwech: Z. Elektrochem., **16**, 369 (1910).
[3] Holwech and Koenig: Z. Elektrochem., **16**, 803 (1910).
[4] Haber and Holwech: Z. Elektrochem., **16**, 810 (1910).
[5] Briner and Naville: Helv. Chim. Acta **2**, 348 (1919); J. Chim. phys. **17**, 329 (1919).
[6] Final Report Nitrogen Products Committee, p. 241 (1920).

of 50 per cent of oxygen to the air supply and that a further increase of about 25 per cent is obtained if the furnace is operated under an absolute pressure of about half an atmosphere."

Data are not available covering equilibrium concentrations of nitric oxide obtained through a large current range and through a wide variation in reduced pressure for various mixtures of oxygen and nitrogen.

(b) Thermal vs. Electrical Equilibria.

For long the question has been in the minds of investigators in this field as to whether the reaction between nitrogen and oxygen in the electric arc is a typical reversible reaction conforming to the requirements of the law of mass action. The reader is referred to the resume given by Knox[1] of the literature prior to the year 1921. Suffice it to say that the work of Muthman and Hofer,[2] LeBlanc and Nuranen,[3] Grau and Russ,[4] Foerster,[5] and Lee and and Beyer,[6] with luminous arcs at ordinary pressures, indicated that this reaction is of a purely thermal nature and that the mass action law holds. Le Blanc and Nuranen and also Grau and Russ, used various mixtures of nitrogen and oxygen and obtained values for equilibrium constants which agreed fairly closely.

On the other hand, Warburg and Leithauser[7] and Berthelot[8] showed definitely that nitric oxide may be produced by the action of the silent discharge on air. Since the experiments were carried out at ordinary temperature, the formation of nitric oxide under these conditions was attributed to electrical influences. Haber and his co-workers,[9] sought to show by the use of cooled, high tension, alternating current arcs at reduced pressures that the primary action is an electrical one—that the kinetic energy of the gaseous ions and of the electrons in the arc is utilized directly in the production of NO and that an "electrical equilibrium" may be secured and to which the mass law does not apply. Haber and Koenig obtained at a pressure around 140 mm., a concentration of 9.8% NO from air, 12.1% from "invert air" (4 vols. oxygen and 1 vol. nitrogen) and 14.4% with a mixture of equal volumes of these gases. They believe that if the temperature of the arc becomes too great then the thermal influences obscure the primary electrical effect.

Only recently, Daniels, Keene and Manning[10] have made the following very important statement in regard to thermal and electrical equilibria of reactions in an electric discharge:

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[1] Knox: "Fixation of Atmospheric Nitrogen," 2d Edition (1921).
[2] Muthman and Hofer: Ber., **36**, 438 (1903).
[3] Le Blanc and Nuranen: Z. Elektrochem., **13**, 297 (1907).
[4] Grau and Russ: Z. Elektrochem., **13**, 345, 573 (1907).
[5] Foerster: Z. Elektrochem., **12**, 536 (1906).
[6] Lee and Beyer: Z. Elektrochem., **13**, 701 (1907).
[7] Warburg and Leithauser: Ann. Physik, **20**, 743 (1906); **23**, 209 (1907).
[8] Berthelot: Ann. Chim. Phys., (8) **9**, 145 (1906).
[9] Haber and Koenig: Z. Elektrochem., **13**, 725 (1907); **14**, 689 (1908); Haber, Koenig and Platou: **16**, 789; Haber and Platou: 796 (1910).
[10] Daniels, Keene and Manning: Trans. Am. Electrochem. Soc., **44**, 247 (1923).

"It is essential to register a strong reservation in regard to the use of the word 'temperature' as applied to an electrical discharge. Ames,[1] among others, has pointed out that one cannot speak properly of the temperature of a mass of distributed molecules of this kind. In an electrical discharge certain molecules acquire an electrical charge and are moved with high velocity in the electrostatic field. Free electrons are moved with still greater velocities. Other molecules in the path are ionized by collision and are given accelerated velocities by the field, so that regions of high kinetic energy result. This high velocity of the molecules and ions is equivalent to a high temperature, but the distribution of velocities does not follow Maxwell's distribution law. It is not possible then to ascribe a definite temperature to the discharge, or even to smaller regions within it, and much less to a single molecule or ion.

"The classical controversy as to whether the formation of nitric oxide in the arc is a purely thermal process or an electrical phenomenon becomes then superfluous. Qualitatively, it is proper to consider an arc as a region of high temperature, but thermodynamic calculations based on a definite temperaature determines the thermodynamic equilibrium of the gases which leave the arc. It is evident that the concentration of endothermic compounds in the electrical field, may be much greater but it cannot be calculated quantitatively because a definite temperature cannot be ascribed to it. Furthermore, it is of little practical importance anyway, for the products cannot be removed without going through this region of lower kinetic energy, where a real equilibrium with a lower concentration of the endothermic compounds is established. For calculations of equilibrium then the temperature should be that of the region immediately surrounding the electrical discharge, but outside of the electrical field. One can say then that an electrical equilibrium exists which gives a higher concentration of the products than the thermal equilibrium."

The above quotation has been given because it states clearly the point of view taken by the writers regarding the temperature of a high tension arc. No attempt will be made in this paper to ascribe a definite thermodynamic temperature within the electrical field of the arc.

Description of Apparatus

(A) Electrical Equipment

The source of power, transformer and electrical measuring instruments were the same as those used in previous work by Tartar and Perkins.[2]

(B) The Arc Furnaces

1. Furnace No. 1.

This furnace was the same as used in the former investigation. It was employed in making experiments on the yield of fixed nitrogen at reduced pressure and also in obtaining equilibria at atmospheric pressure.

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[1] Ames: Bull. Am. Inst. Min. and Met. Eng., p. 2482 (1919).

[2] Tartar and Perkins: J. Phys. Chem., 30, 395 (1926).

2. Furnaces No. 2, 3 and 4.

These furnaces were used in the study of equilibria. The first furnace used in preliminary experiments is shown in Fig. 1. The electrodes of heavy copper wire forming a "horngap," were tightly fitted into a rubber stopper which in turn was fitted to a forty liter carboy. The stopper was also provided with inlet and exhaust tubes. The arc formed was of a flaming type, starting at the point at which the electrodes were closest together, running up the electrodes and finally breaking, whereupon a new arc was started.

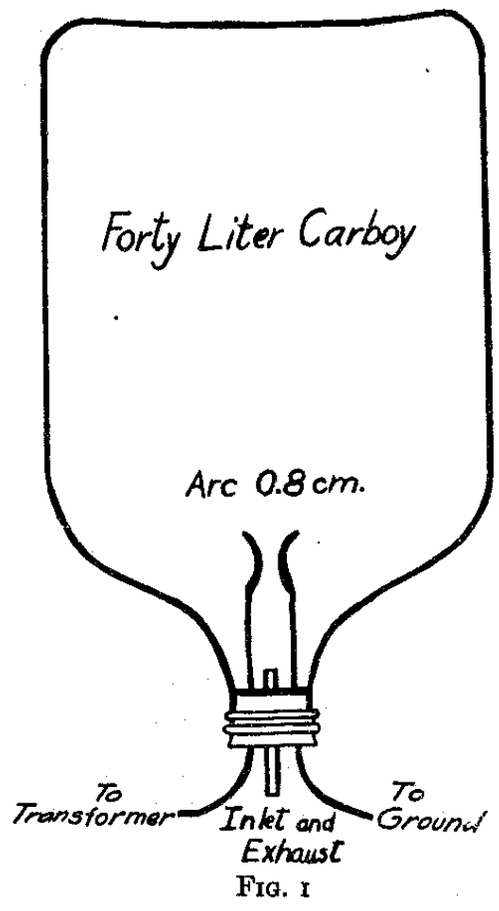


FIG. 1

Furnace No. 3 was similar in construction to that shown in Fig. 1, except that inlet and exhaust tubes were fitted into the neck of a five-liter flask through a rubber stopper. The "horngap" electrodes were nicrome wire and were sealed into the neck of the flask at a distance of about 0.8 cm. from each other. The burning arc was continuous, playing constantly between two points upon the electrodes.

Furnace No. 4 consisted of a five-liter Pyrex flask having platinum "horngap" electrodes sealed into the neck of the flask; see Fig. 2. The distance between the electrodes was about 0.8 cm. The neck of the flask was drawn out and sealed to a three way cock, connected to a manometer and to the apparatus for the absorption of the oxides of nitrogen. The tubulation in the bulb was connected to the gas supply and to a Cenco Hivac Pump, which served to obtain the desired pressures. This furnace was very satisfactory as it could be operated successfully over wide variations in pressure and in current.

(C). The Gas Apparatus and Method of Procedure.

The general arrangement of the gas apparatus used with Furnace No. 1 was the same as that used by Tartar and Perkins.[1]

The arced gases were sampled in different ways, namely: by vacuum flasks, by an adsorption train or in some few preliminary experiments when the sampling carboy was used for the furnace chamber itself (Fig. 1.)

The vacuum flasks or bottles were of a capacity of from 12 to 20 liters with narrow necks fitted with stoppers. The absorption train, consisted of six cylinders 3 cm. in diameter and 25 cm. high, each fitted with inlet and outlet tubes and connected in series with the furnace.

[1] Loc. cit. (See Figs. 2 and 3).

Vacuum flasks were used when the gas was passed but once through the arc at reduced pressure, a procedure which is here designated as "a direct run" at reduced pressure.

In other experiments, the gas was confined in a closed system and circulated repeatedly through the arc until equilibrium was reached, here designated as "a closed cycle run." A 12 to 20 liter bottle served as a gas reservoir and was connected in a closed circuit with the arc furnace, the flow meter and a small "Cenco" positive acting rotary pump. A tube containing phosphorus pentoxide was inserted into the circuit to remove any traces of water. The pump was equipped with a by-pass or shunt. By varying the rate of flow of the gas through the by-pass the desired velocity of the gas through the closed cycle was easily controlled.

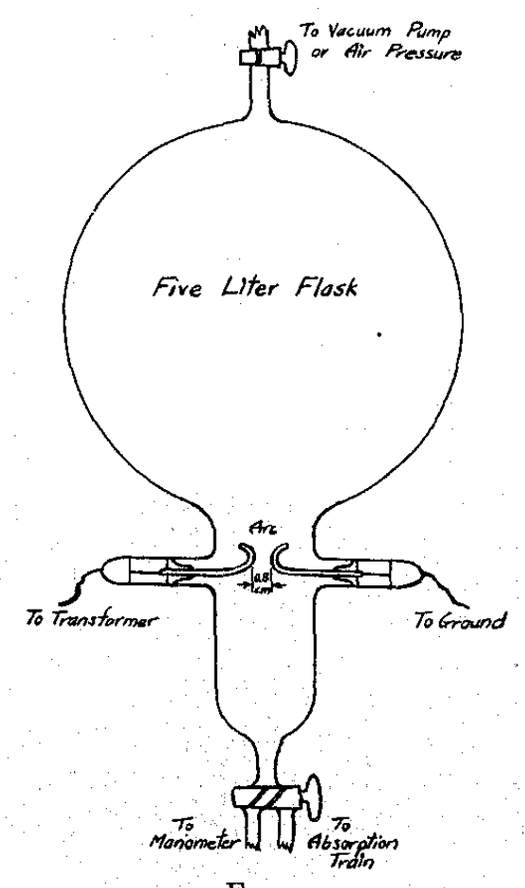


FIG. 2

The method for carrying out the direct runs at reduced pressure and the closed cycle runs at atmospheric pressure were the same as in the previous work.

Many experiments were performed in which equilibrium was reached with the gas at reduced pressure. These experiments will be referred to as "reduced pressure equilibrium runs." The furnace was evacuated to the desired pressure after the gas mixture (nitrogen and oxygen) had been introduced. When the gas mixture was not air, the arc furnace flask was evacuated to a calculated pressure and brought to atmospheric pressure by admitting oxygen and re-evacuating to the desired pressure. When equilibrium was reached (maximum concentration of NO in gas coming from the arc), the furnace and its contents were allowed to come to room temperature amd pressure and temperature readings were again taken. The gas in the furnace was then analyzed by passing the entire gas content through the absorption train.

Methods of Analysis

(a) Analysis of Samples taken with the Vacuum Flask.

The vacuum flasks were highly evacuated prior to taking the samples. The gas sample was taken over a considerable period of time in order to keep the pressure at the arc at the desired value. The temperature and barometric pressure were recorded. After the vacuum flask had been removed from the circuit, the pressure was allowed to come to atmospheric pressure, and water and a known volume of hydrogen peroxide solution were added. The vacuum

flask was then allowed to stand over night. Potassium hydroxide solution was then added and the entire contents of the flask was washed into a liter beaker, boiled to decompose the hydrogen peroxide, cooled and titrated with standard acid, using methyl red as the indicator. Analyses of samples taken with closed cycle runs at atmospheric pressure were made in a similar manner.

(b) Analysis of Solutions from the Absorption Train.

The first two towers were filled with a known volume of hydrogen peroxide solution (3%), and the last three with a known volume of standard alkali. This manner of filling the towers was found to be the most satisfactory as no "fogging" was produced. Absorption of nitrous gases in alkaline solutions of hydrogen peroxide was found to be difficult, while the method employed gave satisfactory results. Advantage was taken of the fact that hydrogen peroxide in dilute solution quantitatively oxidizes nitrous acid to nitric acid.[1] It was found that less than 10 per cent of the total absorption takes place in the last three towers.

At the conclusion of a run, the tower solutions were washed into a liter beaker, boiled to decompose the excess of hydrogen peroxide and made acid with standard acid. The beaker and its contents were then cooled, made alkaline by the addition of standard alkali, and titrated with standard sulfuric acid using methyl red as the indicator.

Litmus, methyl orange, and phenolphtalein are all decolorized by traces of nitrous acid but methyl red is only very slowly acted upon by this acid.[2]

Direct Runs at Reduced Pressure

Tartar and Perkins[3] showed that as the pressure in the arc furnace was reduced, there was a gradual reduction both in the concentration of nitric oxide produced and in yield of fixed nitrogen per kilowatt-hour. They employed a furnace which at atmospheric pressure gave the technical yield of 60 grams nitrogen (as nitric acid) per kilowatt-hour with a constant gas flow of 200-250 liters per hour. For a given rate of gas flow, (calculated to standard conditions) the velocity of the particles through the arc chamber increased with the reduction in pressure. At a pressure of 150 mm., the particles were swept through the furnace at a velocity nearly five times as great as when the same quantity of gas was passed through at 760 mm.

Consequently a series of experiments were made reducing the rate of flow of gas through the arc as the pressure was diminished in order to keep the velocity of the particles of gas through the arc constant.

These runs were made in the following manner: two stopcocks were inserted in the gas line; one immediately before the arc furnace and the second after the exit. The tube from the second stopcock was connected to a large capacity vacuum pump. By careful adjustment of the stopcocks, the rate of flow of gas and the pressure were easily controlled.

[1] Baeyer and Villiger: Ber., **34**, 755-62 (1901).
[2] Koehler, Marqueyrol and Jovinet: Ann. Chim. anal., **18**, 45 (1913).
[3] Tartar and Perkins: J. Phys. Chem., **30**, 595 (1926).

Samples of the gas were taken at the exit of the furnace by the vacuum flask method, employing large bottles of 12 to 20 liters capacity provided with tightly fitting stoppers. Large flasks were necessary in order to secure sufficient quantity of gas for analysis. The bottles were thoroughly dried, evacuated to a small fraction of a millimeter of pressure and then connected to the gas line. The stopcock was then opened slowly and the gas permitted to flow in until the pressure within the bottle was the same as that in the arc furnace. The temperature and pressure at time of sampling were recorded.

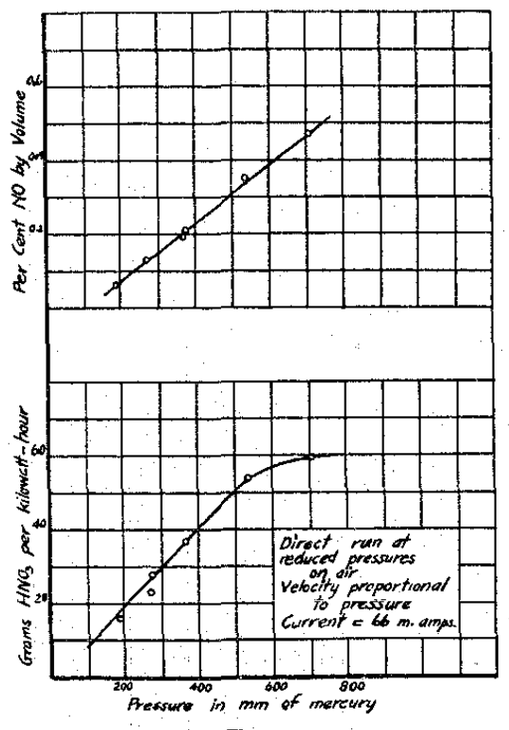


FIG. 3

The experimental data for the reduced pressure runs are reported in Table I and graphically represented in Fig. 3.

These results show that there was a gradual decrease both in the concentration of the nitric oxide and in the yield per kilowatt-hour as the pressure was reduced. As will be shown later, it is possible to build up very high concentrations of nitric oxide at reduced pressures but *no results were obtained indicating that a decrease in pressure may be utilized for securing a greater efficiency in yield by the arc process.*

TABLE I

Results of Direct Runs at Reduced Pressures

Exp. No.	At Electrodes			Velocity of gas thru arc. (Liters per hr. std. Cond.)	Pressure in Arc Chamber (mm. of Hg.)	Nitric Oxide (Percent by volume).	Nitric Acid (HNO_3) (gms. per kw.-hr.)
	Current in Milli-amperes.	Approx. Voltage	Watts Corrected for Trans-former losses				
8 a	66.4	1900	77.3	356.8	706	0.47	59.6
4 a	65	1510	59	258	535	0.35	53.7
7 a	67	1250	50	171.9	371	0.21	37.3
5 a	65.5	1225	47	177.8	366	0.19	36.9
11 a	66.2	1030	44	129.1	273	0.13	27.7
9 a	67	870	38.6	96.3	271	0.13	22.8
6 a	67.8	800	36.3	86.7	188	0.063	15.8

Equilibrium Runs with Air at Atmospheric Pressure without Circulation of Gases

A series of runs was made with air in order to determine the effect of current upon the equilibrium concentration of nitric oxide produced in the electric arc without circulation of the gas other than that caused by the variation in temperature in different parts of the system. The apparatus is shown in

Fig. 1. The arc produced was similar to the type used in the Pauling process for nitrogen fixation; running up the horn-gap and breaking, whereupon a new arc was started at the point at which the electrodes were closest together. Copper electrodes were used.

Runs were made as follows: The carboy was thoroughly dried and the stopper and electrodes inserted. It was then evacuated, filled with conditioned air and the arc was started. Barometric pressure and temperature readings were taken at the beginning and end of the runs. When equilibrium had finally been attained, the arc was stopped and the carboy and contents allowed to come to room temperature. Water and a known volume of hydrogen peroxide solution (3%) were then admitted, the electrodes removed and the carboy was allowed to stand overnight. Standard potassium hydroxide solution was then added, the contents of the carboy was washed into a liter beaker, the solution boiled to decompose the excess hydrogen peroxide and titrated with standard acid using methyl red as the indicator.

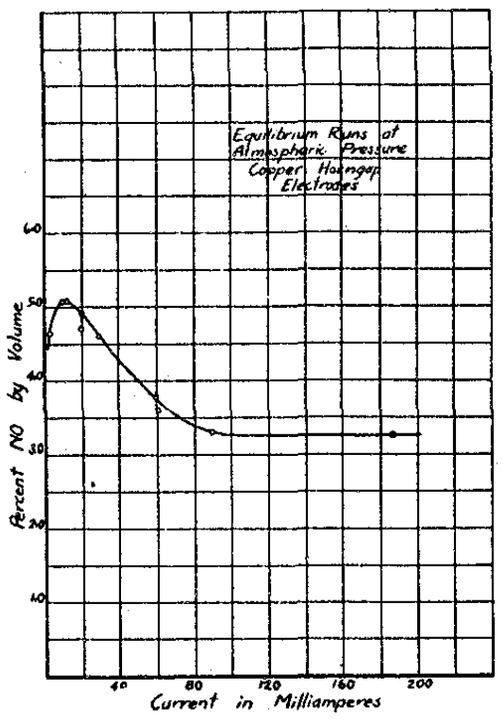


FIG. 4

The experimental data secured from these equilibrium runs at atmospheric pressure are reported in Table II and graphically represented in Fig. 4.

TABLE II

Equilibrium Runs with Air at Atmospheric Pressure

Exp. No.	Secondary Current (In Milli-amperes)	Per Cent Nitric Oxide (By Volume)	Exp. No.	Secondary Current (In Milli-amperes)	Per Cent Nitric Oxide (By Volume)
13 b	3	4.64	10 b	31	4.64
9 b	10	5.08	11 b	61	3.79
7 b	12	5.08	5 b	61	3.61
8 b	20	4.92	1 b	88	3.30
12 b	20	4.69	2 b	90	3.28
14 b	30	4.55	3 b	92	3.36
6 b	30	4.6	15 b	187	3.26

It will be noted that a maximum concentration of nitric oxide of about 5.1 per cent was produced with a current of 10 to 12 milliamperes and the concentration decresaed for both increases and decreases in the value of the current. For lower values of current the arc was not able to build up this concentration and for higher values apparently the temperature gradient from the arc was decreased so that this higher concentration was lessened

by the thermal effects of the arc. The same equilibrium concentration was obtained for values of current above 90 milliamperes, indicating that the temperature gradient for the higher current arcs was the same.

Closed Cycle Runs with Air at Atmospheric Pressure

In the preceding set of experiments a maximum concentration of nitric oxide was produced with the furnace gas in a comparatively static condition, the only motion of the gases being due to the rise of the hot gases from the arc. The next set of experiments was undertaken to show maximum concentration which could be built up with gases passing through the arc with considerable velocity. Equilibrium was attained by passing the gases continuously around a closed sytem composed of the Furnace No. 1, large sample bottle, pump as used by Tartar and Perkins.[1]

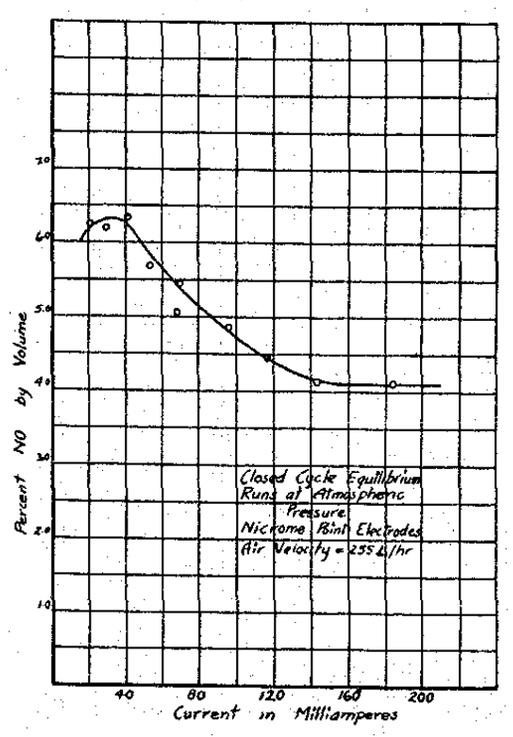


FIG. 5

The arc played between points of nicrome wire. The velocity of the gas through the furnace was 255 liters per hour. Runs were made as follows: The dried sample bottle filled with conditioned air was connected into the system and the circulating pump started. The by-pass valve was then adjusted to give the desired gas velocity and the arc was then started. Readings of barometric pressure and room temperature were taken. When equilibrium had been attained the sample bottle was removed and the contents analyzed.

Very erratic results were obtained at first due to the presence of traces of moisture in the system. This was remedied by inserting a long tube in the closed cycle system containing phosphorus pentoxide. The experimental results are arranged in Table III and presented graphically in Fig. 5.

As in the previous set of experiments the maximum concentration was produced with a small value of current (about 30 milliamperes), decreasing with increase and decrease of current. For high values of current the concentration was again constant.

Another set of closed cycle experiments utilizing electrodes of nicrome formed into a horn-gap, (See Fig. 6) and a gas velocity of 113 liters per hour, gave results very similar to the preceding set, except that somewhat lower concentrations were obtained. These results are also recorded in Table III and in Fig. 7.

The results given in Tables II, III show that the equilibrium concentration of nitric oxide was dependent both upon the current and the ve-

[1] Loc. cit.

TABLE III

Closed Cycle Runs with Air at Atmospheric Pressure

Exp. No.	At Electrodes			Velocity of gas thru arc. Liters per hr.	Nitric Oxide Per Cent by volume
	Current In Milli-amperes	Approx. Voltage	Wats Corrected for Trans-former losses		
9 E	21.0	1920	30.5	255	6.24
8 E	30.0	1430	33	"	6.18
4 E	41.5	2050	68	"	6.34
5 E	53.2	1990	86.5	"	5.68
3 E	68	1920	108.5	"	5.04
2 E	70	1650	98	"	5.46
1 E	95	1420	116.5	"	4.85
6 E	117	1700	161	"	4.44
7 E	143	1830	211	"	4.12
10 E	185	1480	194	"	4.10
17 F	5	—	24	113	2.84
19 F	5	—	24	"	3.24
18 F	7	—	31.5	"	2.93
20 F	10	—	34	"	3.66
15 F	13	4460	35	"	4.01
9 F	20.5	2020	21.5	"	3.61
13 F	28	2300	37	"	5.62
7 F	28	2230	34.5	"	5.95
6 F	40	1910	50	"	4.40
14 F	40	2140	55	"	4.92
10 F	41	1610	41	"	5.14
8 F	50.5	1930	61.5	"	4.69
2 F	62	1770	74	"	4.11
11 F	72	1800	86	"	4.06
1 F	91	1850	113	"	3.80
3 F	116	1410	111	"	3.68
4 F	145	1400	137	"	3.48
12 F	170	2270	258	"	3.34

locity of the gas through the furnace. The higher concentration obtained by circulating the gas was due evidently to a steeper temperature gradient just outside the arc which gave less opportunity for the decomposition of nitric oxide. The concentrations of NO with the quietly burning, "static" arc with current 100-200 milliamperes were about the same as obtained by Tartar and Perkins[1] for equilibrium with a small whirling arc of the Schönherr type and an air velocity of 200 to 600 liters per hour.

[1] Loc. cit.

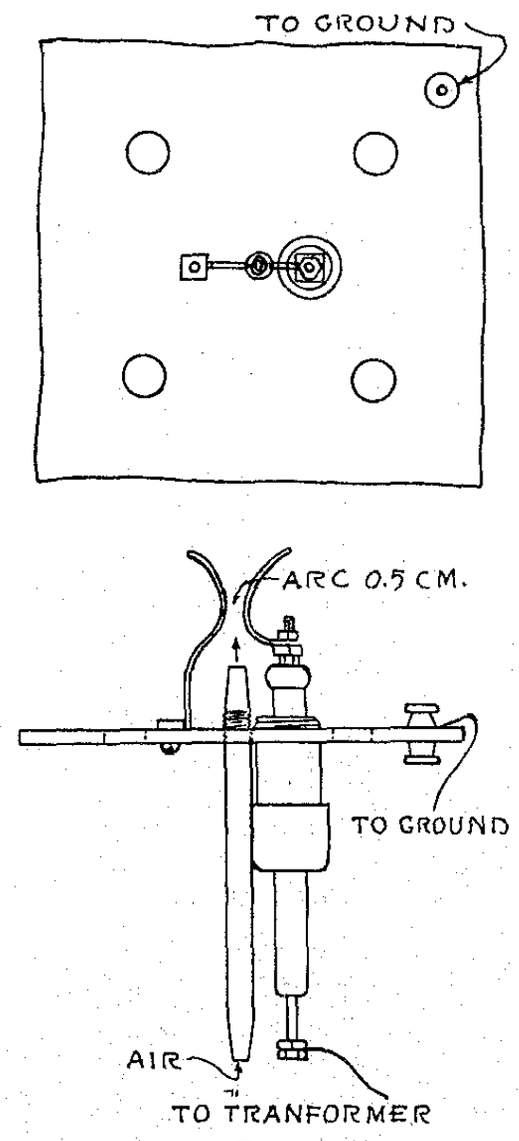


FIG. 6

Equilibrium Runs at Reduced Pressures

The furnaces previously used were not satisfactory for determining equilibrium at reduced pressures due to the fact that a high vacuum could not be maintained over a considerable length of time. Furnace No. 3 was made for preliminary work. It consisted of nicrome horn-gap electrodes sealed into the neck of a five-liter Pyrex flask fitted with a rubber stopper holding inlet and outlet tubes. The inlet reached to the bottom of the flask, so that the contents could be readily blown out into the absorption train. The stopper was covered with sealing wax in order to maintain the vacuum. The rubber exposed to the oxides of nitrogen was not affected in the absence of moisture.

In these preliminary runs, air was the only gas mixture used. The furnace chamber was evacuated to the desired pressure and the arc started. Barometric pressure and room temperature readings were taken at the start and finish of the run. At the conclusion of the run, the furnace was allowed to come to the temperature of the room, dry air was introduced to bring the pressure to atmospheric and

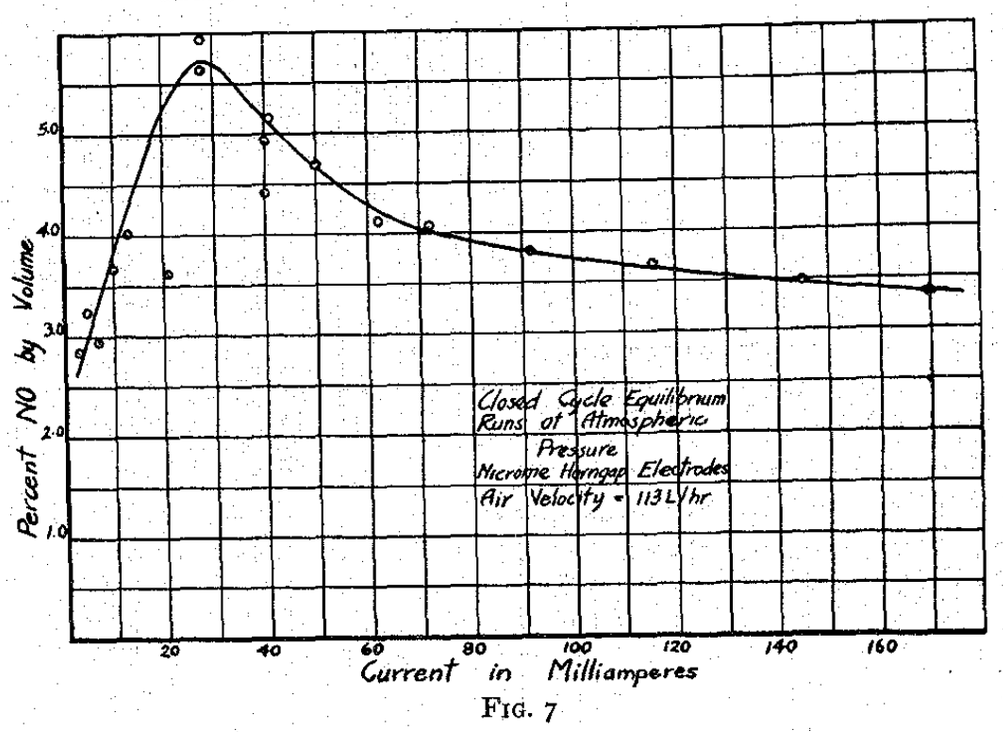


FIG. 7

the gas content was then blown through the absorption train. Two series of runs were made namely for currents of 39 and 66 milliamperes. The experimental data are arranged in Table IV and shown graphically in Fig. 8.

TABLE IV

Equilibrium Runs with Air at Reduced Pressure

Exp. No.	At Electrodes			Arc Pressure mm. of Hg.	Nitric Oxide Per cent by volume
	Current in Milli-amperes.	Approx. Voltage	Watts Corrected for trans-former losses		
10 I	40	390	13.5	119	3.93
2 I	38.7	410	13.5	160	4.92
7 I	40.3	430	15	189	5.40
5 I	38.7	430	14	200	5.71
8 I	40.1	460	15.5	251	6.45
6 I	39	490	16	346	7.03
3 I	39.2	510	16.5	392	6.11
4 I	38.8	520	16.5	401	6.78
1 I	38.8	610	20	561	6.07
6 J	66	390	22	106	3.97
5 J	66.5	410	23	141	5.26
7 J	65	420	23.5	198	6.61
8 J	66	430	24.5	287	7.60
9 J	65.7	460	26	406	7.50
10 J	65.7	500	28	476	6.96
11 J	64.6	540	30	591	6.57
12 J	65	580	32.5	733	5.6

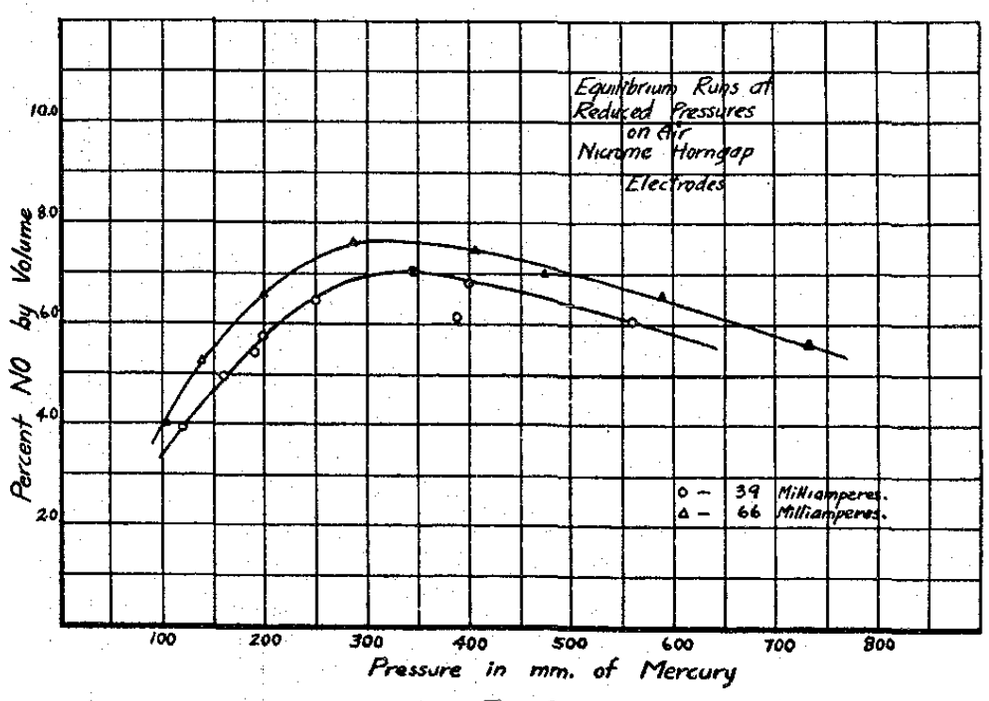


FIG. 8

It is readily seen that a higher concentration of NO by volume was obtained at the higher current value and at a lower pressure.

Furnace No. 4 (Fig. 2) was then constructed in order to more accurately investigate the various factors influencing the obtainable concentration of NO from the arc.

Runs were made as in the previous set of experiments except that mixtures other than air were used. In the latter case the furnace chamber was evacuated to the calculated pressure, brought to atmospheric pressure by admitting dried oxygen, and re-evacuated to the desired pressure. This method insured the same mixture of initial gases.

Series of runs were made upon air with currents of 39, 65, 92, 126, 156 and 190 milliamperes; upon invert air (4 vols. of oxygen and 1 vol. of nitrogen) with currents strengths of 39, 92, and 190 milliamperes and upon a 50-50 nitrogen-oxygen mixture with current strengths of 92 and 190 milliamperes. These runs were made with increasing value of current in order to determine the maximum concentration which could be produced by the arc used. The experimental data are recorded in Tables V, VI and VII and represented graphically, in Figs. 9, 10, and 11.

TABLE V

Equilibrium Runs with Air at Reduced Pressures: Current 39 to 190 Milliamperes

Exp. No.	At Electrodes			Arc Pressure, in mm. of Hg.	Nitric Oxide Per cent by Volume
	Current in Milliamperes	Approx. Voltage	Watts Corrected for Transformer losses		
2 M	39.0	490	16	162	5.22
8 M	39.0	530	17.5	195	5.37
10 M	39.1	540	18	200	5.62
12 M	39.3	570	19	210	5.64
11 M	39.0	650	21.5	255	6.31
1 M	39.5	620	20.5	259	6.69
13 M	39.5	720	22	294	6.39
6 M	39.0	730	22.5	294	6.57
4 M	39.0	740	24.5	354	6.42
7 M	38.8	770	24.5	409	6.11
9 M	39.3	840	26.5	480	5.68
5 M	38.9	960	29.5	540	5.37
3 M	38.0	1060	32.5	612	4.86
1 L	62	370	20	71	5.28
17 L	63	390	21.5	96	5.34
11 L	64	410	22.5	114	4.91
2 L	62	460	24.5	163	6.12
3 L	63	520	28	264	6.91
8 L	62	530	28	267	7.23
14 L	64	590	32	343	6.45

TABLE V (continued)

Exp. No.	At Electrodes			Arc Pressure in mm. of Hg.	Nitric Oxide Per cent by Volume
	Current in Milli-amperes	Approx. Voltage	Watts. Corrected for Trans-former losses		
12 L	62.5	600	31.5	368	6.30
15 L	64	630	34	419	5.95
13 L	63	640	33.5	429	5.70
16 L	62.5	670	35	462	5.94
9 L	62.5	660	34	474	5.98
10 L	62.5	720	37	573	5.46
7 L	62	730	37.5	634	5.00
8 K	94	410	33	71	5.88
7 K	91	430	32.5	103	5.93
10 K	90	470	34.8	155	6.94
9 K	91	500	37.5	206	7.56
13 K	91	500	38	216	7.30
11 K	92	530	40	253	7.04
3 K	92	550	42	288	6.54
12 K	90	570	43	365	6.06
4 K	91	600	45.5	406	5.68
5 K	92	610	47	473	5.41
6 K	92	670	50.5	602	5.12
7 Q	126	480	48	77	7.58
6 Q	127	500	52	110	7.98
5 Q	127	520	53	146	8.28
8 Q	128	540	55	171	7.92
4 Q	126	540	55	197	7.63
1 Q	126	590	61	287	6.10
2 Q	126	620	65	353	5.54
3 Q	126	660	68	469	5.11
5 R	156	510	62	58	8.06
3 R	154	520	61	93	8.64
6 R	156	510	62.5	94	8.36
7 R	156	540	65.5	124	8.16
2 R	154	540	65.5	140	8.15
4 R	156	550	68.5	161	8.05
3 S	188	510	73	73	8.15
5 S	189	520	76	88	8.26
2 S	192	530	78	94	8.79
4 S	186	520	74	96	8.69
9 S	191	560	81	124	8.22
1 S	185	540	76	127	8.35
7 S	188	550	80	135	8.35

TABLE VI

Equilibrium Runs with Invert Air: Current 39, 92 and 190 Milliamperes

Exp. No.	At Electrodes			Arc Pressure in mm of Hg.	Nitric Oxide Per cent by Volume
	Current In Milliamperes	Approx. Voltage	Watts Corrected For Transformer losses		
9 O	40.6	420	14.5	104	5.82
7 O	40.6	470	16	150	7.94
6 O	40.0	500	16.5	193	8.20
10 O	40.3	650	22	223	7.93
8 O	40.0	600	21	238	7.56
5 O	39.7	680	23	261	7.45
4 O	40.1	740	25	319	6.70
1 O	39.3	800	27.5	390	6.13
3 O	38.4	830	27	450	5.94
8 N	93	420	32	92	7.94
11 N	92.5	460	35	126	8.93
2 N	92	470	35.5	159	8.77
9 N	93	480	38	176	8.62
10 N	92.5	490	37.5	184	8.92
6 N	93	500	38.5	209	8.71
4 N	95	520	42.5	251	7.81
7 N	93	540	43.5	308	6.94
1 N	91	590	45.5	399	6.09
3 N	92	640	50	472	5.90
5 N	93	670	54	568	5.31
1 U	186	525	75	96	12.27
2 U	190	525	76	99	12.1
3 U	188	540	78	124	11.1
4 U	192	520	77	74	11.0

An examination of the curves shown in Fig. 9 shows that the pressure at which a maximum concentration of NO was obtained was variable and dependent upon the current through the arc. For a current of 39 milliamperes the maximum concentration was obtained at a pressure of about 320 mm., for 65 milliamperes at about 260 mm., for 92 milliamperes at about 210 mm., for 126 millamperes at about 150 mm. and for 190 millamperes at 100 mm. of mercury. Moreover the equilibrium concentration increased with the increase of current until a value of 8.8 per cent NO by volume was obtained. This was the maximum concentration attainable with the arc.

Fig. 10 shows that for the higher pressure both air and invert air gave about the same concentration but below a pressure of 350 mm. of mercury this was no longer true. If the law of mass action is applicable to the reaction

$$N^2 + O_2 = 2\ NO$$

air and invert air should have given the same equilibrium concentration.

Apparently the law is approximately valid for the higher pressures that is, where thermal properties predominate in the arc.

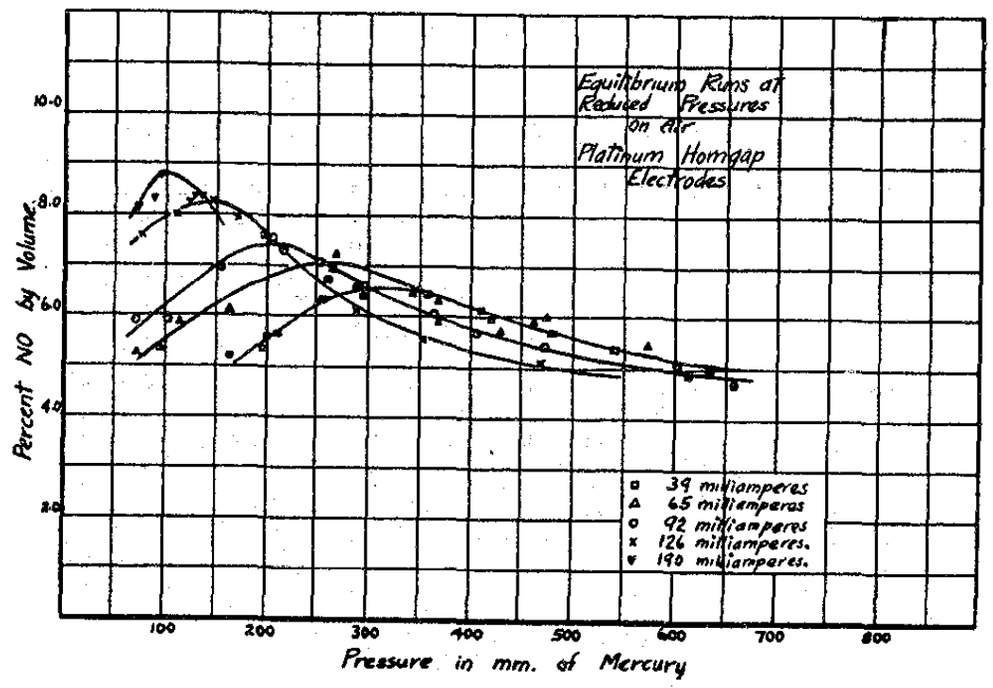


FIG. 9

TABLE VII

Equilibrium Runs with Mixture of Equal Volumes of Nitrogen and Oxygen

Exp. No.	At Electrodes			Arc Pressure mm of Hg.	Nitric Oxide Per cent by Volume
	Current In Milli-amperes	Approx. Voltage	Watts Corrected For Trans-former losses		
8 P	93.5	460	36	109	11.66
9 P	93	480	36.5	129	11.91
6 P	94	490	38.5	156	12.51
11 P	92.5	490	37.5	155	11.94
10 P	92	490	37.5	174	11.6
2 P	93	550	43	257	9.19
7 P	93	610	48	364	7.39
4 P	92.5	660	51.5	463	6.75
5 P	92	750	59	587	5.91
3 T	190	520	76	72	12.39
1 T	188	520	74	97	13.0
2 T	185	540	76	109	12.62
4 T	189	540	78	100	13.17

In Fig. 11, equilibrium concentrations of NO are represented for the three gaseous mixtures employed namely: air, invert air, and equal volumes of oxygen and nitrogen. The law of mass action would require that the equal

volume mixture should give a concentration of 25% in excess of that of air or invert air. This was approximately true at the higher pressures, but at the reduced pressures the deviation was marked.

The results secured within the pressure range 100-150 mm. are in general accord with the findings of Haber and Koenig.[1]

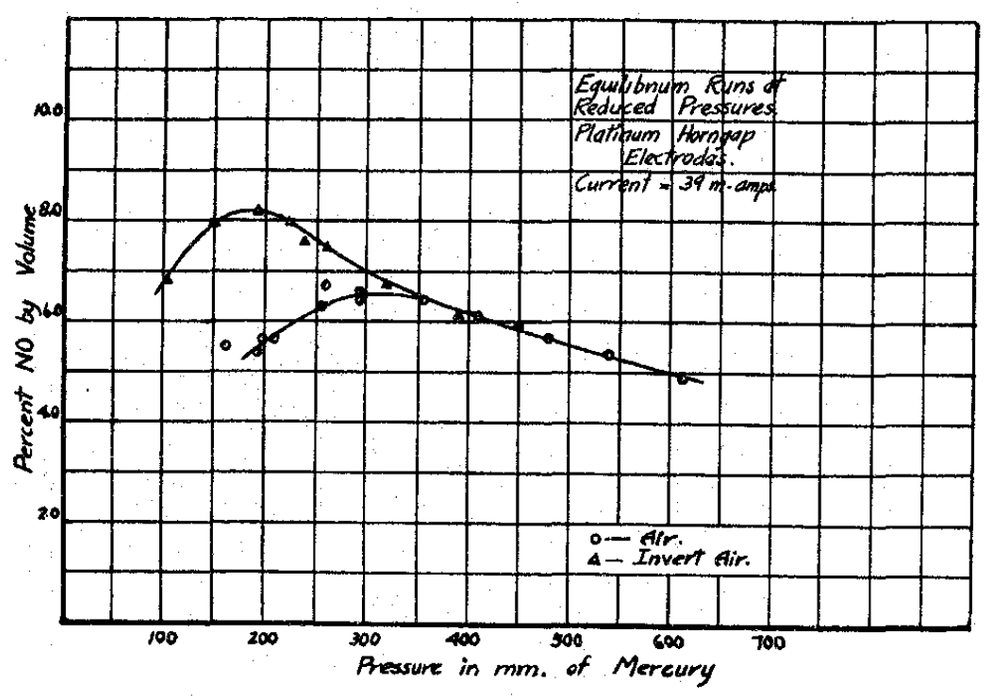


FIG. 10

The data on the equilibria obtained with air and invert air may be used to give an idea regarding the temperature gradient and the rapidity of cooling at the edge of an arc without artificial circulation of the gas. Approximately six per cent of nitric oxide (see Tables V and VI and Figs. 10 and 11) was formed with both air and invert air at half an atmosphere using currents of 39 and 92 milliamperes. This concentration of NO was evidently in thermal equilibrium with the gas immediately outside the arc filament at the particular temperature at which the equilibrium was "frozen." By extrapolation from their experiemental data, Nernst, Finckh and Jellinek[2] estimate that the temperature corresponding to a thermal equilibrium concentration of six per cent NO is approximately 3500° Abs. The velocity of the decomposition of nitric oxide has been investigated by Jellinek[3] for the temperature range 689° to 1750° C. From this reaction constant and the equilibrium constant of the reaction, the reaction constant for the formation of nitric oxide can be determined. From these data the rates of formation and decomposition of NO in a given mixture can be calculated.[4]

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[1] Loc. cit.

[2] Nernst, Finckh and Jellinek: Z. anorg. Chem., **45**, 111, 126 (1905); **49**, 213, 229 (1906).

[3] Jellinek: Z. anorg. Chem., **49**, 263 (1906).

[4] For details concerning the formulation and method of calculation the reader is referred pp. 134, Bulletin 2041, U. S. War Dept.; Report on the Fixation and Utilization of Nitrogen.

The estimated time required for the decomposition at 3500° Abs. of 40 per cent of the nitric oxide present in an air mixture containing initially twice the amount of this substance that will be present when equilibrium is established, is 1.1×10^{-8} seconds. At 1900° and 1770° Abs. the times required for this amount of decomposition are 2.5 and 21 minutes respectively. The gas from the arc zone should surely be cooled very quickly to at least 1900° Abs. to "freeze" the equilibrium. Below this temperature the rate of decomposition will be sufficiently slow that the gas may be cooled less rapidly without appreciable loss of combined nitrogen. These values indicate that in order to

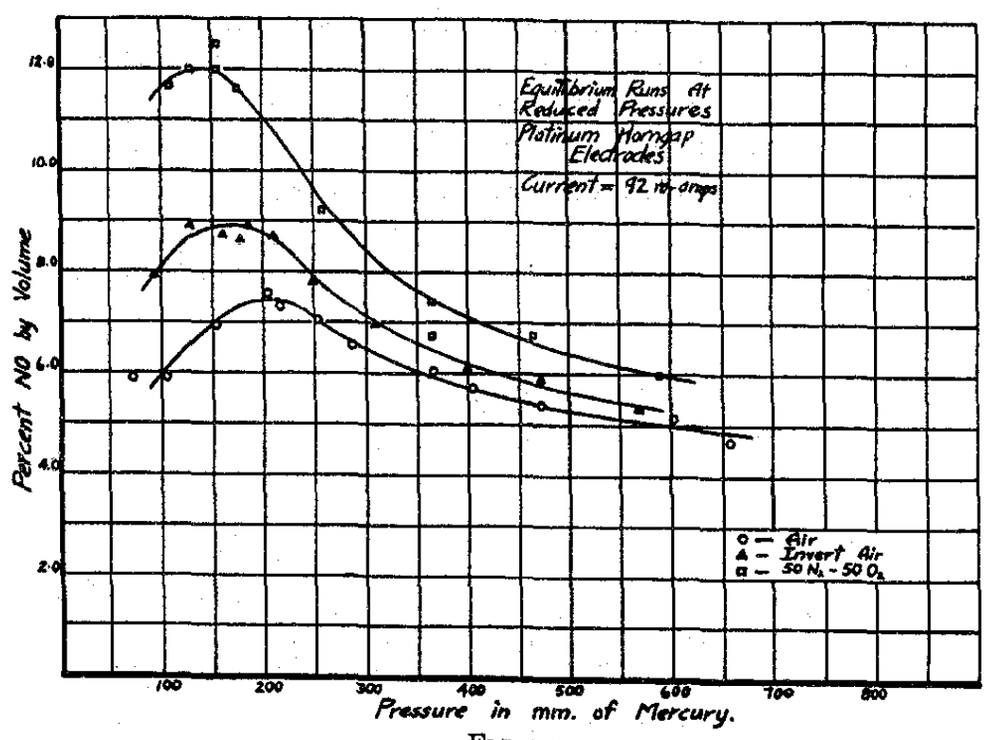


FIG. 11

"freeze" the equilibrium in the gases coming from the arc at 3500° Abs. there must be an abrupt drop in temperature within an extremely short distance of about 1600°. Also that even from a quietly burning arc the equilibrium is "frozen" with a rapidity that is almost incredible. The writer realizes that the reaction velocities given above were obtained by extrapolation from experimental data secured at lower temperatures. Nevertheless, the conclusion seems justified at least when gases are passed through the arc with considerable velocity the approximate equilibrium concentration of nitric oxide at the high temperature in the immediate vicinity of the arc is secured without appreciable decomposition. Furthermore, the rapidity with which the equilibrium is "frozen" shows the futility of the efforts of previous investigators to increase the concentration of nitric oxide by bringing the gases after leaving the arc in contact with water-cooled walls.

Acknowledgment

Grateful acknowledgment is made to the E. I. du Pont de Nemours Company for the grant of a fellowship which made this investigation possible.

Summary

1. The use of reduced pressure gave a decrease both in the concentration of nitric oxide and in yield of fixed nitrogen per kilowatt hour.

2. The maximum equilibrium concentration of nitric oxide obtained over a wide range in pressure was dependent upon the current.

3. The effect upon the equilibrium concentration of nitric oxide produced by varying the velocity of the gases was not marked.

4. High concentrations of nitric oxide may be produced in an uncooled high tension, electric arc at reduced pressure.

5. The maximum concentrations of 8.8 per cent for air, 12.2 per cent for invert air and 13.1 per cent for equal volumes of oxygen and nitrogen were obtained at a pressure of about 100 mm. of mercury.

6. The law of mass action holds approximately for the reaction between nitrogen and oxygen in the high tension electric arc at pressures greater than one-half atmosphere.

7. Water-cooling of the gases after leaving the arc is unnecessary.

University of Washington,
Seattle, Washington.

PROPERTIES AT THE ABSOLUTE ZERO OF TEMPERATURE OF THE QUANTITIES ASSOCIATED WITH THE REVERSIBLE MIXING OF SUBSTANCES

BY R. D. KLEEMAN

The quantities associated with the reversible mixing of substances can be shown to possess a number of useful properties at the absolute zero of temperature. They will be deduced directly from results already established[1] which for reference will be given here. If S denote controllable entropy of a substance or mixture at the volume v, absolute temperature T, and pressure p, it was shown that when the substance is under the pressure of its vapor at the absolute zero of temperature, a point called the absolute zero of control.

$$S = 0 \tag{1}$$

$$\left(\frac{\partial S}{\partial T}\right)_v = 0 \tag{2}$$

$$\left(\frac{\partial S}{\partial T}\right)_p = 0 \tag{3}$$

$$\frac{dS}{dT} = 0 \tag{4}$$

and besides

$$\left(\frac{\partial v}{\partial T}\right)_p = 0 \tag{5}$$

$$\left(\frac{\partial^2 v}{\partial T^2}\right)_p = 0 \tag{6}$$

$$\frac{dv}{dT} = 0 \tag{7}$$

$$\frac{d^2 v}{dT^2} = 0 \tag{8}$$

The total entropy, which will be denoted (S), it may be recalled, was divided into an externally uncontrollable part and a controllable part already denoted by S which is a function of v and T. Similarly the total internal energy, which will be denoted by (u), was divided into an uncontrollable part and a controllable part which will be denoted by u.

1. Let us pass a number of substances (which may include mixtures) through the following cycle:

a) Mix the substances in any given state by a reversible process isothermally at the absolute zero of temperature. The increase in the total entropy is $(H_m/T)_{T=0}$, where H_m denotes the heat absorbed.

[1] J. Phys. Chem., **31**, 747-756, 937-967 (1927).

b) Raise the temperature of the mixture to T under any given conditions. The increase in the total entropy is equal to the increase in controllable entropy S.

c) Separate the substances isothermally, which gives rise to an increase in entropy equal to $-H_m/T$.

d) Lower the temperature of the substances to $T = 0$, and reduce them to their initial state. The increase in total entropy is equal to the increase $-\Sigma S_a$ in controllable entropy.

Since the total change in the total entropy is zero, we have

$$S - \Sigma S_a = \Delta S = \frac{H_m}{T} - \left(\frac{H_m}{T}\right)_{T=0} \tag{9}$$

It follows from this equation that H_m cannot be finite when $T = 0$, which would make the term within the brackets infinite since the other terms in the equation are not infinite. Hence we have

$$H_m = 0 \tag{10}$$

when the substances are mixed in *any given state* at the absolute zero of temperature.

This result may also be obtained from the well known equation

$$H_m = T\left(\frac{\partial A}{\partial T}\right)_v \tag{11}$$

where A denotes the external work done during the process of mixing. When $T = 0$ the equation reduces to equation (10).

2. Next let us pass the substances through the following cycle which is similar to the one just given:—

a) Mix the substances by a reversible process isothermally at the temperature T. The total entropy is increased by H_m/T, where H_m as before denotes the heat absorbed.

b) Increase the temperature of the mixture by ∂T at constant volume, which gives rise to an increase in total entropy equal to the increase in controllable entropy ∂S.

c) Separate the substances isothermally from each other, and reduce to their original volumes. This gives rise to an increase in the total entropy equal to $-\frac{H_m + \partial H_m}{T + \partial T}$.

d) Decrease the temperature of the substances by ∂T, keeping their volumes constant. The total entropy is increased by $-\Sigma \partial S_a$ the increase in controllable entropy.

Since the total change in the total entropy is zero we have

$$\partial S - \Sigma \partial S_a + \frac{H_m}{T} - \frac{H_m + \partial H_m}{T + \partial T} = 0$$

or

$$\left(\frac{\partial \Delta S}{\partial T}\right)_v = \frac{1}{T}\left(\frac{\partial H_m}{\partial T}\right)_v - \frac{H_m}{T^2} \tag{12}$$

the suffix v indicating that the volumes of the constituents and mixture are kept constant during a change in temperature.

If the mixing at the beginning of the cycle is carried out with the substances and final mixture under the pressures of their vapors at the absolute zero of temperature, the sum of terms on the left hand side of the equation is zero since each term is separately equal to zero, (equation (2)). The term H_m/T^2 on the right hand side then becomes indeterminate according to equation (10), and since $T = 0$. The value of the right hand side is therefore

$$\frac{1}{T}\left(\frac{\partial H_m}{\partial T}\right)_v - \frac{1}{2T}\left(\frac{\partial H_m}{\partial T}\right)_v$$

according to the Calculus. Since it cannot be infinite we must have

$$\left(\frac{\partial H_m}{\partial T}\right)_v = 0 \tag{13}$$

This still leaves the right hand side indeterminate, and its value is therefore

$$\frac{1}{2}\left(\frac{\partial^2 H_m}{\partial T^2}\right)_v.$$

Since we have just seen that this is zero, we also have

$$\left(\frac{\partial^2 H_m}{\partial T^2}\right)_v = 0 \tag{14}$$

for the heat absorbed during the mixing of a number of substances at the absolute zero of temperature under the pressures of their vapors.

If the foregoing cycle is carried out keeping the pressures of the substances and mixture constant instead of their volumes, the left hand side of the resultant equation, applied to substances initially under the pressure of their vapors at the absolute zero of temperature as before becomes zero (equation (3)). It can then be shown similarly as before that

$$\left(\frac{\partial H_m}{\partial T}\right)_p = 0 \tag{15}$$

and

$$\left(\frac{\partial^2 H_m}{\partial T^2}\right)_p = 0 \tag{16}$$

Again if the foregoing cycle is carried out with the substances and mixture under pressures equal to their vapor pressure respectively, the left hand side of the resultant equation becomes zero at the absolute zero of temperature. (equation (4)). It can then be shown similarly as before that

$$\frac{dH_m}{dT} = 0 \tag{17}$$

$$\frac{d^2 H_m}{dT^2} = 0 \tag{18}$$

where the total differentiation indicates that the substances and mixture are kept under the pressures of their vapors.

3. We have seen in a previous paper that the controllable entropy and internal energy of a substance varies only with v and T, since these are the

only quantities that can be varied. If, however, we are dealing with a number of substances another controllable operation is possible, namely that of mixing the substances. Now although the controllable internal energy and entropy of a substance or mixture according to their definitions are zero when the substance is in the condensed state under the pressures of its vapor at the absolute zero of temperature, it does not follow directly from this that no change in internal energy or entropy takes place on mixing several substances under the same conditions. A further investigation is necessary to determine this, the basis of which is furnished by the foregoing investigation. The change in entropy during the process of mixing is $(H_m/T)_{T=0}$, which assumes an indeterminate form according to equation (10) and since $T = 0$. It can be shown to be equal to zero by means of equation (13), and hence no change in entropy takes place. The internal energy in this connection will be considered in Section 5.

4. We have just seen that the term $(H_m/T)_{T=0}$ is zero, and hence equation (9) may now be written

$$T\Delta S = H_m \tag{19}$$

where S denotes the controllable entropy. This equation holds in general.

If (S) denotes total entropy we have

$$T\Delta(S) = H_m \tag{20}$$

directly from the fundamental principles of thermodynamics. Equation (19) is not a case of the foregoing equation, it should be carefully noted, but its truth had to be proved separately. The two equations give

$$\Delta S = \Delta(S) \tag{21}$$

which expresses that under all conditions the controllable entropy only of a number of substances is changed on mixing them.

Since H_m can often be measured directly and ΔS be calculated from specific heat measurements, etc., equation (19) may be tested experimentally and its truth thus be established.

Equation (21) may be written

$$\frac{\Delta u + A}{T} = \frac{\Delta(u) + A}{T}$$

which reduces to

$$\Delta u = \Delta(u) \tag{22}$$

where (u) denotes total internal energy, u as usual the controllable internal energy, and A the external work done during the mixing.

Since

$$H_m = \Delta(u) + A \tag{23}$$

by definition, we also have

$$H_m = \Delta u + A \tag{24}$$

by means of equation (22), and equation (19) may therefore be written

$$T\Delta S = \Delta u + A \tag{25}$$

an equation involving controllable quantities only and which applies to any temperature.

Similarly the well known equation

$$\Delta(u) = T\left(\frac{\partial A}{\partial T}\right)_v - A \tag{26}$$

may be written

$$\Delta u = T\left(\frac{\partial A}{\partial T}\right)_v - A \tag{27}$$

by means of equation (22), and now involves controllable quantities only.

Since u and S can be calculated from specific heat measurements, etc., and A can in some cases be measured directly, the truth of equations (25) and (27) may be established experimentally.

5. From the definition of the total internal energy we have directly that

$$h_m = \Delta(u) \tag{28}$$

where h_m denotes the internal heat of mixture, or the increase in total internal energy on mixing a number of substances under any given conditions. By means of equation (22) this equation may be written

$$h_m = \Delta u \tag{29}$$

On applying it to the mixing of a number of substances under the pressures of their vapors so that the resultant mixture is under the pressure of its vapor, at the absolute zero of temperature, the right hand side becomes zero since u is zero for each substance according to a previous investigation and hence,

$$h_m = 0 \tag{30}$$

under these conditions. Thus both the total and controllable internal energy are not changed on mixing a number of substances under the stated conditions at the absolute zero of temperature.

6. Since

$$H_m = h_m + A \tag{31}$$

and this equation is applied to mixing under vapor pressure, we have by means of equations (30) and (10)

$$A = 0 \tag{32}$$

under these conditions at the absolute zero of temperature.

On differentiating equation (11) with respect to T at constant volume we obtain

$$\left(\frac{\partial H_m}{\partial T}\right)_v = \left(\frac{\partial A}{\partial T}\right)_v + T\left(\frac{\partial^2 A}{\partial T^2}\right)_v \tag{33}$$

At the absolute zero of control this equation becomes

$$\left(\frac{\partial A}{\partial T}\right)_v = 0 \tag{34}$$

according to equation (13) and since $T = 0$.

On differentiating equation (33) with respect to T at constant volume it becomes

$$\left(\frac{\partial^2 H_m}{\partial T^2}\right)_v = 2\left(\frac{\partial^2 A}{\partial T^2}\right)_v + T\left(\frac{\partial^3 A}{\partial T^3}\right)_v \cdots$$

At the absolute zero of control it gives

$$\left(\frac{\partial^2 A}{\partial T^2}\right)_v = 0 \tag{35}$$

according to equation (14) and since $T = 0$.

According to the Differential Calculus

$$\left(\frac{\partial A}{\partial T}\right)_p = \left(\frac{\partial A}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p + \left(\frac{\partial A}{\partial T}\right)_v \tag{36}$$

At the absolute zero of control this equation becomes

$$\left(\frac{\partial A}{\partial T}\right)_p = 0 \tag{37}$$

according to equation (34) and the equation (5) obtained previously. On differentiating equation (36) with respect to T at constant pressure it becomes

$$\left(\frac{\partial^2 A}{\partial T^2}\right)_p = \left(\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial v}\right)_T\right)_p \left(\frac{\partial v}{\partial T}\right)_p + \left(\frac{\partial A}{\partial v}\right)_T \left(\frac{\partial^2 v}{\partial T^2}\right)_p + \frac{\partial A}{\partial v.\partial T}\left(\frac{\partial v}{\partial T}\right)_p + \left(\frac{\partial^2 A}{\partial T^2}\right)_v \tag{38}$$

At the absolute zero of control it gives

$$\left(\frac{\partial^2 A}{\partial T^2}\right)_p = 0 \tag{39}$$

according to equations (5), (6), and (35).

If the restriction of differentiation at constant pressure is removed from equation (36) it becomes

$$\frac{dA}{dT} = 0 \tag{40}$$

at the absolute zero of control by means of equations (7) and (34).

Again if the restriction of constant pressure is removed from equation (38) it becomes

$$\frac{d^2 A}{dT^2} = 0 \tag{41}$$

at the absolute zero of control by means of equations (7), (8) and (35).

7. From equation (31) and the equations (13), (14), (15), (16), (17), (18), (34), (35), (37), (39), (40), (41) it immediately follows that at the absolute zero of control

$$\left(\frac{\partial h_m}{\partial T}\right)_v = 0 \tag{42}$$

$$\left(\frac{\partial^2 h_m}{\partial T^2}\right)_v = 0 \tag{43}$$

$$\left(\frac{\partial h_m}{\partial T}\right)_p = 0 \tag{44}$$

$$\left(\frac{\partial^2 h_m}{\partial T^2}\right)_p = 0 \tag{45}$$

$$\frac{dh_m}{dT} = 0 \tag{46}$$

$$\frac{d^2h_m}{dT^2} = 0 \tag{47}$$

8. From equations (30), (42) and (43) it follows that close to the absolute zero of temperature

$$h_m = a_1 T^{2+b_1} \tag{48}$$

where a_1 and b_1 are positive constants. This equation and equations (32), (31), and (11) give

$$A = \frac{a_1}{b_1 + 1} T^{2+b_1} \tag{49}$$

and hence according to equation (31)

$$H_m = \left(\frac{b_1 + 2}{b_1 + 1}\right) a_1 T^{2+b_1} \tag{50}$$

If h_m can be expressed as a series of integral powers of T, as is likely, b_1 is equal to unity.

In general for any temperature we will then have

$$h_m = a_1 T^3 + a_2 T^4 + a_3 T^5 + \tag{51}$$

$$A = \frac{a_1}{2} T^3 + \frac{a_2}{3} T^4 + \frac{a_3}{4} T^5 + \tag{52}$$

$$H_m = \frac{3a_1}{2} T^3 + \frac{4a_2}{3} T^4 + \frac{5a_3}{4} T^5 + \tag{53}$$

for substances under their vapor pressures, where a_1, a_2, are functions of v. Since

$$\left(\frac{\partial h_m}{\partial T}\right)_v = \Delta c_v \tag{54}$$

where c_v denotes the specific heat at constant volume, we also have

$$\Delta c_v = 3a_1 T^2 + 4a_2 T^3 + 5a_3 T^4 + \tag{55}$$

In using these series in practice it is necessary to retain at least three terms because at temperatures well removed from zero these quantities do not vary so rapidly as indicated by an individual term.

If the mixing is carried out under any other conditions

$$h_m = X + a_1 T^3 + a_2 T^4 + a_3 T^5 + \tag{56}$$

from which it follows that

$$A = -X + \frac{a_1}{2} T^3 + \frac{a_2}{3} T^4 + \frac{a_3}{4} T^5 + \tag{57}$$

while equation (53) retains the same form, since equation (10) holds for all states at the absolute zero of temperature, where X is a function of v.

In this paper and the preceding two papers quoted, we have confined ourselves almost entirely to the properties of substances and mixtures *under their vapor pressures* at the absolute zero of temperature. Some of the results obtained may be extended to other states at this temperature, which will be given with other results in subsequent papers.

EMULSIFICATION BY SOLID POWDERS*

BY A. J. SCARLETT, W. L. MORGAN AND J. H. HILDEBRAND

Emulsification by means of fine insoluble powders was reported by Ramsden[1] in 1903, and further studied by Pickering[2] in 1907, who worked upon the problem of plant sprays. Although the emulsifying power of fine solids had doubtless been operative in the preparation of various plant sprays for some time previous, this use, even today, has apparently occurred without clear realization, since soaps are usually also added, that the necessarily finely divided insecticide itself may act as an emulsifier. In 1898 Elmore[3] developed the first ore flotation process which took advantage of the ability of some finely powdered ores to act as emulsifiers in certain oil-water systems.

Pickering carried on a large amount of work with powders as emulsifying agents and stated among his conclusions that solid particles, in order to have emulsifying power, must display but a small tendency towards coalescence, must be wet more easily by the aqueous phase than by the oil, and must not be crystalline.

Pickering apparently knew only oil-in-water type emulsions, and it was not generally realized at that time that emulsions may exist of water in oil. Bancroft,[4] in 1912, in reviewing Pickering's work added "Pickering does not point out that a corollary of his hypothesis is that insoluble particles, which are more readily wetted by oil than by water, should tend to promote the emulsification of water in oil." Schlaepfer,[5] following this suggestion, found that lampblack goes into the kerosene layer when shaken with it and water, and that it accordingly gives emulsions of water in oil.

Briggs,[6] also working in the Cornell laboratory, made the following statement: "It is generally agreed that the liquid which wets the solid emulsifier the more strongly under the conditions of the experiment tends to become the outside phase, the less strongly wetting liquid being broken up into drops. Just why this is so, is difficult to explain satisfactorily for the moment."

In 1923 Finkle, Draper and Hildebrand[7] suggested the following mechanism for the explanation of emulsion type. "Many powdered solids have been shown to be capable of stabilizing emulsions. It seems to be possible to account for the type of emulsion produced by the following hypothesis. It is obvious, first, that the powder must collect at the interface in order to be effective. Now, this will occur only when the solid is wetted by both liquids,

*Contribution from the Chemical Laboratory of the University of California.

[1] Ramsden: Proc. Roy. Soc., **72**, 156 (1903).

[2] Pickering: J. Chem. Soc., **91**, 2010 (1907); Kolloid-Z., **7**, 14 (1912).

[3] Elmore: Min. Sci. Press, **113**, 449 (1916).

[4] Bancroft: J. Phys. Chem., **16**, 511 (1912).

[6] Schlaepfer: J. Chem. Soc., **113**, 522 (1918).

[5] Briggs: J. Ind. Eng. Chem., **13**, 1008 (1912); J. Phys. Chem., **24**, 147 (1920).

[7] Finkle, Draper and Hildebrand: J. Am. Chem. Soc., **45**, 2780 (1923).

with a finite angle of contact of the interface with the solid. In general, one liquid will wet the solid better than the other, so that the particles will be drawn more largely into the former. If there are enough solid particles to fill the interface the tendency of the interface to contract will cause it to bend in the direction of the more poorly wetting liquid, which makes it easy for the latter to become the enclosed phase. Of course, a solid in order to behave in this way, must be easily dispersed in the outer liquid, its particles not tending to agglomerate therein or to stick together when serving as protective armor for emulsified drops. One should, therefore, be able to predict whether or not a given solid powder can stabilize an emulsion, and also which liquid will become the dispersed phase by noting the angle of contact of the interface with the solid."

Clayton[8] in his book "Emulsions and Emulsification," which appeared during the same year as the paper by Finkle, Draper and Hildebrand, also stressed the importance of the angle of contact between the liquid interface and the solid emulsifier.

The present investigation was begun with the purpose of examining further into the relation between the contact angle of the liquid interface with the solid, the type and stability of the corresponding emulsion. A large number of such contact angles were measured by observation with the aid of a long-focus microscope provided with eyepiece with attached angular scale and provided with cross hairs. The attempt was then made to check the angles obtained by using the inclined plate method. In this a plane surface of the solid is inclined at such an angle that the liquid interface remains horizontal, as tested by oblique reflection, right up to the solid surface. It was found, however, that a horizontal interface could be maintained over long periods of time with widely different angles of inclination of the plate. An interface which climbs up the plate may be made horizontal either by increasing the inclination of the plate towards the horizontal, or by lowering it with inclination unchanged. It was expected at first that a true equilibrium angle of contact would be approached if sufficient time were allowed, and in order to determine upon which side of the equilibrium value the contact angle might lie a microscope provided with cross hairs was focused upon the line of contact between the interface and the plate in order to observe any rise or fall due to an approach to equilibrium. It was found, however, that the inclination of the plate could be varied over wide angles without giving rise to any movement of the line of contact over periods up to 24 hours. It, therefore, seemed hopeless to attempt any accurate measurement of an equilbrium angle.

It is true that there are rough limits beyond which the angle, in most cases, cannot be varied. Thus a glass plate thoroughly cleaned in chromic acid cleaning solution, washed with conductivity water and dried over a bunsen flame, according to the method recommended by Langmuir,[9] was inserted

[8] Clayton: "Emulsions and Emulsifications" (1923), 1923.
[9] Langmuir: Trans. Faraday Soc., **15**, Pt. 3, 62 (1920).

in a vertical position through a toluene water interface. The water was observed to climb the plate into the toluene so that the interface formed a fairly definite angle with the plate. Upon lowering the plate this angle increased until the interface became horizontal or even depressed somewhat irregularly along the plate, tending, however, slowly to rise above the horizontal surface. It is evidently not possible to maintain for any period an interfacial angle on the water side much greater than 90°. However, when the plate is raised the line of contact may be pulled up so far as to give a zero angle. It was even possible to pull the water film clear up through the layer of toluene. There seemed to be little or no tendency for this film of water to recede, but it seemed gradually to grow thinner, possibly by a solution of water in toluene, and after 24 hours the interface was back near to its original position but with the contact angle still extremely small. It is evident that water can slowly displace toluene from a glass surface, but that the displacement of water by toluene is an extremely slow process.

Anyone who has endeavored to secure dry glass surfaces is aware of the large force which must operate between water and glass. It is hardly surprising, therefore, that the small gravitational field operating at the contact of a liquid interface with a solid should be unable to bring about a rapid approach to equilibrium. We suspect also that the greater difficulty of displacing the wetting liquid is a rather general phenomenon.

To attempt to secure an equilibrium angle by allowing long periods of time introduces the danger of considerable error through the concentration of traces of impurity at the surfaces involved. Since our object was not so much the accurate measurement of contact angles as the correlation of contact angle with emulsion type and stability, since variations of contact angles within zero and 90°, on one hand, and 90° and 180° on the other hand, would appear to have no great significance, and finally since the important matter is the contact angle under the actual conditions under which the emulsion is prepared, we turned to a direct demonstration of the existence of the mechanism which had earlier been postulated, namely, the microscopic examining and photographing of various emulsions.

The emulsions were obtained by shaking the two liquids with the solid powder in a test tube. No attempt was made to secure uniformity in the size of the particles since occasional large particles provide better opportunity for observing the protrusion of the solid into the outer liquid. The photographs were made with a 16 mm. objective and the magnification secured was 100 diameters. In the case of benzene emulsions it was often found desirable to place a ring of vaseline as a seal around the edge of the cover glass to prevent evaporation and shift of position during exposure. In the case of emulsions with water as the internal phase it is necessary to prevent wetting of the microscope slide and cover glass by water, which can be done by wiping it with kerosene. Since the depth of focus of the microscope was in general less than the depth of the emulsion viewed, even when the larger globules were flattened by the cover glass, it is impossible to bring all the particles into sharp focus at once. We therefore focused upon the particles around the

edge of each droplet. Figs. 1–6, although representing a variety of emulsifying agents and both types of emulsion, all indicate very clearly, first, that the powder is collected at the interface, and, second, that the particles protrude largely into the outer liquid indicating better wetting and smaller angles of contact. This is particularly striking in the case of the occasional larger particles.

Fig. 1 represents an emulsion of benzene and water. It was found here, in accordance with our experiments with glass plates previously given, that in order for the glass powder to be held at the interface it was necessary first to drive off adsorbed water by heating, and then to wet the powder with benzene before adding water. Even so, a great deal of it goes completely into the water phase but sufficient is held at the interface to give a very satisfactory emulsion.

A similar variability in wetting power was encountered on using copper dust to emulsify benzene in water. A strip of copper covered with a film of grease is wetted better by benzene than by water and the interface is therefore depressed at the copper surface, forming an angle of practically 180° on the water side. On cleaning the metal in concentrated NH_4OH solution, and drying, an angle of less than 90° is obtained, water wetting the copper better than benzene. Ordinary electrolytic copper dust cannot be wetted by water alone even when triturated in a mortar; when benzene is added, the dust goes into the benzene layer and a film forms on the benzene side of the interface. On shaking violently, bags of benzene are formed, filled with imperfectly protected globules of water emulsified in benzene. If the copper dust is first treated with hot NH_4OH solution and then washed with water, it is readily wetted by the water and then forms a stable emulsion of benzene in water, illustrated in Fig. 2. Powdered copper, formed by reduction of copper oxide by hydrogen, was readily wetted by water and gave only benzene-in-water emulsions. Clean copper, like glass, when pulled up through the interface benzene-water will hold a film of water which resists displacement by benzene. Therefore, as in the case of glass, the most stable emulsion of benzene in water was formed by drying the cleaned dust and then wetting it with benzene before adding the dispersing liquid water.

Fig. 3, representing toluene emulsified in water by powdered pyrite, is particularly striking in showing that the angle of contact of the interface with the solid is less than 90° on the water side. Fig. 4, showing benzene emulsified in water by zinc dust, is somewhat less striking on account of the absence of large particles but clearly shows the same relations. Fig. 5, illustrating water emulsified in kerosene by powdered willow charcoal, and Fig. 6, showing water dispersed in benzene by mercuric iodide, are interesting as illustrating the reverse type of emulsions.

We will give finally certain additional observations showing the connection between type of emulsion and magnitude of contact angle, the latter obtained by lowering a surface polished on c'oth-covered wooden wheels using carborundum of increasing fineness. Polishing was followed by washing by a strong stream of water free from grease, followed by drying in the sun.



FIG. 1
Benzene emulsified in water by glass powder.

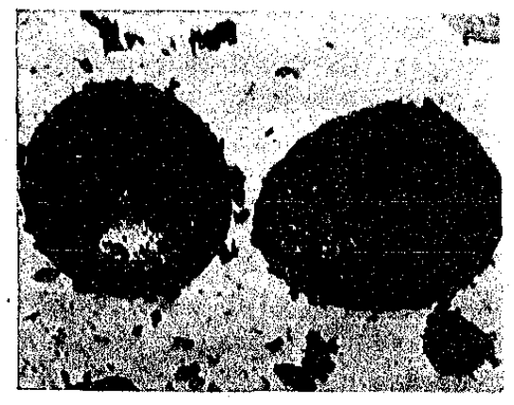


FIG. 2
Benzene emulsified in water by copper powder, cleaned by ammonia then by water

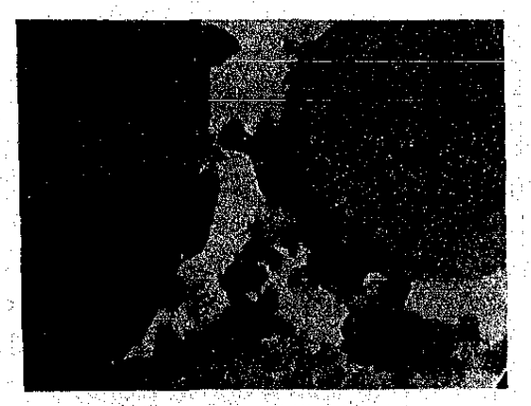


FIG. 3
Toluene emulsified in water by powdered pyrite



FIG. 4
Benzene emulsified in water by zinc dust



FIG. 5
Water emulsified in kerosene by powdered charcoal

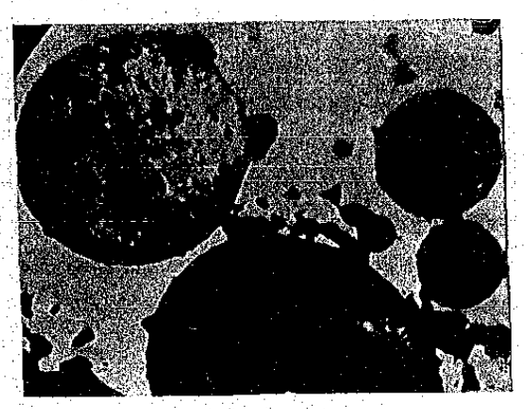


FIG. 6
Water emulsified in benzene by powdered mercuric iodide

The following solids all produced an interfacial angle of contact less than 90° on the water side, and their powders stabilized emulsions of benzene and water; magnesite, calcite, gypsum, barite, quartz, fluorite, corundum, sphalerite, zinc,[1] pyrite.[1] Bromobenzene and ether were also emulsified in water by powdered fluorite, and the interface gave the corresponding angle of contact. Heptane was emulsified in aniline by powdered sodium chloride which was observed also to be wet better by the aniline.

Angles of contact of a benzene water interface greater than 90° on the water side were observed with charcoal, mercuric iodide, lampblack, [6, 7, 10] (coating upon a glass plate) and sulfur,[1] all of which give emulsions in which water is dispersed. The same situation was found with water, heptane and benzoic acid.

In conclusion we wish to supplement the explanation previously given to account for the direction of curvature of a liquid interface contaminated by a solid powder, by suggesting that in the preparation of an emulsion there may be produced initially droplets of either liquid in the other, those droplets, however, in which the adsorbed powder projects largely into the interior are but poorly protected against coalescence with similar droplets, whereas the droplets upon which the adsorbed projects largely into the interior phase are very effectively protected. The relative wetting of the emulsifying agent by the two liquids thus accounts for the type of emulsion produced both by promoting curvature of the interface in one direction rather than in the other, and providing protection for droplets of the one liquid far superior to that afforded droplets of the other.

Summary

Difficulties in the way of determining angles of contact between liquid interfaces and solids are reported and discussed.

Demonstration of the connection between the interfacial contact angle and the type of emulsion is given by means of microphotographs of emulsions stabilized by solid powders.

In addition to the explanation for this connection previously given showing how the angle of contact favors film curvature in one direction, it is further suggested that in forming the emulsion droplets having the particles chiefly on the outside of the interface would be better protected from coalescing than those having the particles more on the inside.

[10] Moore: J. Am. Chem. Soc., **41**, 940 (1919).

19 - 138

A STUDY OF THE THERMAL DECOMPOSITION OF NITROGEN PENTOXIDE[1]

BY F. O. RICE AND DOROTHY GETZ[2]

The field of reaction rate investigation has been very fruitful in producing an extensive literature on the theory of chemical reactivity. Of all reactions, first-order, homogeneous gas reactions are perhaps theoretically the most interesting. From time to time various gaseous decompositions have been reported as unimolecular, but further work has usually shown them to be either heterogeneous or multimolecular. Within the past year, however, several new reactions have been brought forward as unimolecular.[3]

At the time the present investigation was undertaken, the thermal decomposition of nitrogen pentoxide held the unique position of "sole survivor of the group of truly monomolecular reactions".[4] The velocity of this reaction has been measured under a wide variety of conditions, and, with two exceptions, has always conformed to the original values obtained by Daniels and Johnston. The initial pressures of the pentoxide have been varied over wide limits with no effect on the specific reaction rate except in the work of Hirst and Rideal who found a velocity five times the normal value when the total gas pressure was below about .25 millimeters, the rate falling off to normal as the pressure increased due to the decomposition. The effect of the presence of various gases whether inert, such as argon and nitrogen, or whether decomposition products such as oxygen and nitrogen tetroxide, has been studied and the gases found to be without influence on the velocity. However,

[1] Contribution from the Chemical Laboratory of the Johns Hopkins University.

[2] Extracts from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Hinshelwood and Hutchison: Proc. Roy. Soc., **111** A, 245 (1926); Hinshelwood and Thompson: **113** A, 221 (1926); Hinshelwood: **114** A, 84 (1927); Smith: J. Am. Chem. Soc., **49**, 43 (1927); Ramsperger: **49**, 912 (1927).

[4] It seems desirable to include a bibliography of the experimental work on nitrogen pentoxide. Unmarked citations in the text refer to this list.

(a) Daniels and Bright: J. Am. Chem. Soc., **42**, 1131 (1920). Vapor Pressure.
(b) Daniels and Johnston: Ibid., **43**, 53 (1921). Thermal Decomposition.
(c) Daniels and Johnston: Ibid., **43**, 72 (1921). Photochemical Decomposition.
(d) Lueck: Ibid., **44**, 757 (1922). Thermal Decomposition in Solution.
(e) Wulf, Daniels and Karrer: Ibid., **44**, 2398 (1922) Oxidation of N_2O_4 by O_3. Daniels, Wulf and Karrer: Ibid., **44**, 2402 (1922). Decomposition of N_2O_5 in Presence of O_2.
(f) White and Tolman: Ibid., **47**, 1240 (1925). Initial Rate of Decomposition.
(g) Hunt and Daniels: Ibid., **47**, 1602 (1925). Decomposition at Low Concentration.
(h) Daniels: Ibid., **47**, 2856 (1925). Infra-red Absorption Spectra.
(i) Hirst: J. Chem. Soc., **127**, 657 (1925). Thermal Decomposition.
(j) Hirst and Rideal: Proc. Roy. Soc., **109** A 526 (1925). Decomposition at Low Pressures.
(k) Daniels: J. Am. Chem. Soc., **48**, 607 (1926). Infra-red Radiation and N_2O_5.
(l) H. A. Taylor: Ibid., **48**, 577 (1926). Infra-red Radiation and N_2O_5.
(m) F. O. Rice: Ibid., **48**, 2099 (1926). The Catalytic Activity of Dust Particles.
(m) Fazel and Karrer: Ibid., **48**, 2837 (1926). Photochemical Decomposition.
(o) Norrish: Nature, **119**, 123 (1927). Decomposition of N_2O_5
(p) Busse and Daniels: J. Am. Chem. Soc., **49**, 1257 (1927). Effect of Foreign Gases.
(q) Bodenstein: Z. physik. Chem., **104**, 51 (1923). Decomposition of N_2O_5.

arguments have been advanced for and against autocatalytic activity of the dioxide, the strongest evidence for such an effect being the remarkable retardation of the decomposition of the pentoxide observed by Daniels, Wulf and Karrer in the presence of excess ozone. Their experimental results have not been confirmed by other workers.

In view of the theoretical importance of the reaction, of the fact that all other so-called unimolecular reactions up to that time had been found to be heterogeneous or multimolecular on rigorous investigation, and particularly in view of the very interesting results of Daniels, Wulf and Karrer, it seemed worth while to undertake another study of the reaction. Hence we decided to investigate the thermal decomposition of nitrogen pentoxide from two standpoints, namely, (1) the reaction may be heterogeneous; (2) the reaction may be homogeneous but multimolecular, involving a catalyst.

The effect of dust in promoting both the thermal and the photochemical decomposition of hydrogen peroxide has been experimentally demonstrated in this Laboratory.[1] It seemed possible that this reaction might also be due to the catalytic effect of dust—in this case possibly phosphorus pentoxide dust. A survey of the literature lends weight to this hypothesis, since, as far as one can judge from the experimental details given by Wulf, Daniels and Karrer, phosphorus pentoxide dust was probably absent to a far greater extent in their work than in any other. Further, their experiments are the only ones showing any inhibition of the decomposition of nitrogen pentoxide, an inhibition which at the present time is still unexplained. Consequently we tried both to remove dust from the gases entering the decomposition chamber, using asbestos and electrical filters, and to add dust by placing phosphorus pentoxide directly in the decomposition tube.

On the other hand, if the decomposition of nitrogen pentoxide is due to the presence of some catalyst, that catalyst must be some compound which is present in constant amount since widely separated groups of investigators working under different conditions have in general obtained consistent unimolecular constants. Since phosphorus pentoxide has been almost universally used for the preparation of nitrogen pentoxide or for drying purposes, it might be a possible source of some positive catalyst. Further, there is the possibility of nitric acid itself being the catalyst. Since theoretically no reaction goes to completion, there must always be a trace of nitric acid present when the pentoxide is prepared or dried in the usual way. By drying the nitrogen pentoxide at different temperatures such an effect would be revealed since the equilibrium concentration of the nitric acid would be changed. Another method of testing for the presence of an accidental trace of catalyst is to prepare the nitrogen pentoxide by an entirely new method such as from the action of chlorine on silver nitrate; by following this method we eliminated altogether the use of phosphorus pentoxide in the preparation of nitrogen pentoxide.

[1] Rice and Reiff: J. Phys. Chem , **31**, 1300; Rice and Kilpatrick: 1400 (1927).

Experimental

The nitrogen pentoxide used throughout most of the work was prepared from nitric acid obtained by distilling under a partial vacuum a mixture of four parts of concentrated sulphuric acid with one part of concentrated nitric acid. This practically 100% nitric acid was then dehydrated by means of phosphorus pentoxide and the crude nitrogen pentoxide distilled off and dried completely by distillation back and forth through phosphorus pentoxide as often as necessary.

In the experiments on the decomposition of gaseous nitrogen pentoxide the method of Hunt and Daniels was followed although there were certain modifications in the apparatus. The reaction tube was about 1 cm. in diameter and about 87 cm. in length. This tube was kept at constant temperature very efficiently by using a specially constructed double-jacketed condenser through which circulated the vapors from boiling methyl alcohol contained in a distilling flask. A return tube rendered the heating system automatic. The condenser was carefully wrapped in asbestos to exclude light and minimize heat losses. Two thermometers, one inserted at each end of the condenser, gave a constant check on the temperature.

Several experiments were carried out in the usual way in order to have a check on the results obtained when the filters, etc. were introduced into the system. A stream of nitrogen after passing through drying towers and a flowmeter, entered the tube containing the nitrogen pentoxide which was protected with phosphorus pentoxide guard tubes and kept at 0°C. The resulting mixture of gases streamed through one of these guard tubes cooled with ice, into the decomposition chamber and thence through two test tubes containing standard sodium hydroxide. The results were as follows:

TABLE I

Ordinary Runs on the Decomposition of N_2O_5*

Expt.	Mols N_2O_5 Taken	Mols N_2O_5 Decomposed	Time Min.	T°C.	Observed k calculated to 65°C.
1.	.002347	.001018	2.123	64.4	.286
2.	.002402	.001015	2.120	64.4	.276
3.	.002193	.000977	2.194	64.6	.281
4.	.002165	.000967	2.193	64.6	.282
5.	.001948	.000937	2.471	64.5	.281
6.	.001979	.000948	2.467	64.5	.279

*Daniels and Johnston obtained .286 for the calculated value of the velocity constant at 65°C. and .292 for the observed.

We first tried to remove dust from the nitrogen pentoxide by means of asbestos filters. After preliminary experiments we decided to use South African blue asbestos according to the directions of Scott.[1] A filter was prepared from some blue asbestos wool and sealed to the apparatus between the reaction tube and the phosphorus pentoxide guard tube. Two runs were made, but no change in the velocity constant was effected.

[1] Scott: J. Ind. Eng. Chem., 14, 432 (1922).

TABLE II

Runs using a Blue Asbestos Filter

Expt.	Mols N_2O_5 Taken	Mols N_2O_5 Decomposed	Time Min.	T°C	Observed k calculated to 65°C.
1.	.002115	.000944	2.269	64.5	.282
2.	.001993	.000901	2.226	64.5	.286

An electrical filter was next constructed.[1] The filter resembled a small sealed-in Pyrex condenser. The inner central tube carried the high-tension wire which was made of three lengthwise strands of copper wire from copper gauze with the crosswise strands cut very close, the whole being given several axial turns throughout its length. The outer jacket was provided with inlet and outlet tubes for the pentoxide and was wrapped with copper gauze and grounded. The filter was operated by an induction coil. In preliminary distillations in a current of oxygen no perceptible decomposition was observed qualitatively during the passage of the nitrogen pentoxide through the filter. Several experiments were carried out with the electrical precipitator sealed to the reaction tube. The nitrogen pentoxide was contained in a small tube without phosphorus pentoxide guard tubes. A current of oxygen was used in these experiments. No change in the velocity constant was observed.

TABLE III

Runs using an Electrical Precipitator

Expt.	Mols N_2O_5 Taken	Mols N_2O_5 Decomposed	Time Min.	T°C.	Observed k calc. to 65°C.
1.	.002109	.000934	2.435	63.9	.271
2.	.001943	.000911	2.474	64.0	.285
3.	.001947	.000898	2.472	64.0	.279

Another set of experiments was then carried out with the apparatus arranged as originally described, only in these phosphorus pentoxide was introduced directly into the decomposition tube. On the one hand, in all these experiments we had large quantities of dust directly in the reaction tube; on the other hand, we certainly had any catalyst present which might be connected with the use of phosphorus pentoxide, but we could detect no specific effect, even though here the pentoxide was at 65° C. and in preceding experiments in which guard tubes were used the phosphorus pentoxide in the guard tube leading to the decomposition tube had been kept at some temperature between room temperature and 0°C. by partially cooling the tube with ice. The results are given in the table below.

We thought it would be interesting to see if a platinum surface in the reaction tube would have any effect. Consequently several platinum foil electrodes with wires attached were distributed throughout the length of the decomposition chamber. No alteration in the velocity constant was obtained.

[1] See Lamb, Wendt and Wilson: Trans. Am. Electrochem. Soc., **35**, 357 (1919); Tolman, Reyerson, Brooks and Smyth: J. Am. Chem. Soc., **41**, 587 (1919).

TABLE IV

Runs with Phosphorus Pentoxide in the Reaction Tube

Expt.	Mols N_2O_5 Taken	Mols N_2O_5 Decomposed	Time Min.	T°C.	Observed k calc. to 65°
1.	.001778	.000817	2.488	64.1	.272
2.	.001718	.000791	2.492	64.1	.273
3.	.002243	.001066	2.454	64.3	.287
4.	.002296	.001099	2.453	64.3	.284
5.	.002241	.001038	2.485	64.1	.276
6.	.002221	.001029	2.488	64.1	.276

TABLE V

Runs with Platinum Electrodes in the Reaction Tube

Expt.	Mols N_2O_5 Taken	Mols N_2O_5 Decomposed	Time Min.	T°C	Observed k calc. to 65°C.
1.	.002237	.001073	2.471	64.4	.282
2.	.002277	.001081	2.468	64.4	.279

Nitrogen pentoxide was next prepared in a different way, eliminating phosphorus pentoxide entirely.[1] The crystals were made by passing chlorine over silver nitrate, a method which was essentially that of Deville[2] though certain modifications were introduced.

The apparatus was arranged as follows. A three-way stopcock leading from nitrogen and chlorine cylinders was sealed to a series of three large U tubes containing glass beads and concentrated sulphuric acid. A trap was placed between these drying tubes and two U tubes containing pulverized silver nitrate sifted over glass beads. These were followed by a filter of glass wool, a tube for collecting the crystals, a similar tube used as a trap and two more large U tubes containing glass beads and concentrated sulphuric acid. Both tubes containing silver nitrate were heated for about two hours by oil baths kept at about 150°C., a current of nitrogen passing through the apparatus meanwhile. The crystals of pentoxide formed when chlorine was slowly passed over the silver nitrate were collected in a tube chilled by ice and salt. It was found necessary to heat the tubes to a rather high temperature to start the reaction and then to hold the temperature around 60°C. After the reaction was completed oxygen dried by passing through concentrated sulphuric acid and an empty tube chilled with carbon dioxide snow and ether, was swept over the crystals. By regulating the temperature at which the crystals were kept, all of the yellow liquid in the tube with the pentoxide was eventually volatilized, and the crystals themselves were then distilled into the next tube which had not been needed as a trap. Part of the time an oxygen current containing a very small amount of ozone was used. The crystals were white and well-formed.

[1] We wish to thank Dr. J. C. W. Frazer for suggesting and helping with this experiment.

[2] Deville: Ann. Chim. Phys. (3) **28**, 241 (1850).

Several runs were made with these crystals. Calcium chloride towers, concentrated sulphuric acid and an empty tube surrounded by carbon dioxide snow and ether sufficed to dry the oxygen or nitrogen used, since all phosphorus pentoxide was carefully eliminated. The velocity constants, however, were the same.

TABLE VI

Runs on Nitrogen Pentoxide prepared from Silver Nitrate and Chlorine

Expt.	Mols N_2O_5 Taken	Mols N_2O_5 Decomposed	Time Min.	T°C.	Observed k calculated to 65°C.
1.	.001933	.001061	2.870	64.4	.296
2.	.001939	.001034	2.868	64.4	.284
3.	.001905	.001033	2.873	64.4	.290
4.	.001873	.001024	2.878	64.4	.293

It is quite certain that a little moisture reached the crystals due to some mishaps in sealing the tubes together, etc., but it seems hardly possible that chance would introduce exactly the same amount of nitric acid as might have been present in the preceding work when phosphorus pentoxide was used in the preparation and drying of the crystals. Moreover, oxygen dried as described above, was swept through the apparatus for some time before the measurements were made. Of course the merest trace of nitric acid might suffice to serve as a catalyst. However, the crystals were next distilled directly into phosphorus pentoxide prepared by the method of Finch and Fraser.[1] Before making the following runs the nitrogen pentoxide was distilled into the usual crystal-collecting tube equipped with phosphorus pentoxide guard tubes. Moreover, the decomposition tube had similar guard tubes sealed to each end. The velocity constants remained the same.

TABLE VII

Runs on Nitrogen Pentoxide after Treatment with Phosphorus Pentoxide

Expt.	Mols N_2O_5 Taken	Mols N_2O_5 Decomposed	Time Min.	T°C.	Observed k calculated to 65°C.
1.	.001887	.001058	2.887	64.6	.298
2.	.001834	.001011	2.876	64.7	.288
3.	.001812	.001024	2.877	64.7	.299
4.	.001996	.001026	2.598	64.7	.287
5.	.001976	.000991	2.603	64.7	.276

Decomposition in Solution.

Lueck first investigated the velocity of the decomposition of nitrogen pentoxide in solution. He discovered the remarkably interesting fact that the rate in carbon tetrachloride and in chloroform closely approximates that found by Daniels and Johnston in the gas phase. The only measurements made on the decomposition of the pentoxide in solution naturally have been carried out in organic solvents. We thought it would be very interesting to

[1] Finch and Fraser: J. Chem. Soc., 129, 117 (1926).

see what would happen in 100% nitric acid itself provided the 100% nitric acid should be sufficiently stable under experimental conditions to render only a comparatively negligible correction necessary.

The method of attack planned consisted in running two samples on the nitric acid—nitrogen pentoxide solution. One was to be carried to complete decomposition at a temperature of 65° C., the other to approximately half-life at 35° C. Each sample was to be analyzed for nitrite content, which would give all the necessary data for calculation of the velocity constant after applying one correction for the nitrite originally present in the sample and another for any decomposition of the nitric acid itself. Such decomposition would, of course, not only increase the nitrite content of the sample, but also continually change the concentration of the pentoxide.

This method was successfully applied to a solution of nitrogen pentoxide in carbon tetrachloride. A sample of Eastman's best-grade carbon tetrachloride was introduced into a tube which was then sealed off at the inlet end. The tube was sealed to a long tube of phosphorus pentoxide which was in turn connected with a receiver carrying phosphorus pentoxide guards and a separate inlet tube through which samples could later be withdrawn. After chilling the contents of the distilling vessel with ice and salt, the whole system was evacuated. By then keeping the receiver in ice and salt and the distilling vessel at room temperature the distillation proceeded very slowly and quietly. The receiver was then sealed to a tube provided with phosphorus pentoxide guards and containing nitrogen pentoxide crystals. The nitrogen pentoxide was introduced into the carbon tetrachloride by sending a nitrogen stream through the flowmeter system and over the crystals at 0°C.

A sample of the solution was drawn up into the decomposition vessel and the inlet sealed off. The decomposition vessel consisted of a piece of capillary tubing bent in the form of a U. Just above the bend in one arm of the U a bulb of approximately 1 or 2 cc. capacity had been blown. At some distance above the bulb this arm was bent twice at right angles and drawn out to a long slender delivery tube which was immersed in acidified standard potassium permanganate solution contained in a test tube. The other shorter arm of the U was similarly bent and drawn out in order to facilitate the filling of the tube and the delivery of the sample for analysis after heating. One sample was carried to complete decomposition by heating for twenty or twenty-five minutes in the vapor of boiling methyl alcohol. A second sample was heated to approximately one-half decomposition in the vapor of boiling ether. Some nitrogen dioxide always escaped from the bulb at 35°C. and a great deal came over at 65°C. rendering the test tube guard absolutely essential. A third sample was analyzed for nitrite originally present.

The constant in the first experiment may be slightly low because no such escape of nitrogen dioxide as actually took place was expected, and probably a little dioxide was lost. The constants obtained by using this method were found to agree with those of Lueck's. If, instead of determining the initial concentration of nitrogen pentoxide by permanganate titration of the totally decomposed sample, a total acidity was run on an unheated sample,

the constants approached the calculated value of Daniels and Johnston. One possible explanation of the discrepancy is loss of pentoxide as well as dioxide from the decomposition tube. However, these results are quite interesting considering the simple rough and ready method.

TABLE VIII

Decompostion of Nitrogen Pentoxide in Carbon Tetrachloride

Expt.	Mols N_2O_5 originally present per g. soln.	Mols N_2O_5 decomposed per g. soln.	Time of heating in Min.	T°C.	Observed k calculated to 35°C.**
1.	.0000854	.0000438	90	34.4	.00867
2.*	.0000886	.0000367	77.2	34.2	.00772
3.*	.0000886	.0000444	105	34.2	.00737
4.	.0000718	.0000352	75	34.5	.00961
5.	.0000718	.0000423	105	34.5	.00905
6.*	.0000829	.0000352	75	34.5	.00788
7.*	.0000829	.0000423	105	34.5	.00758

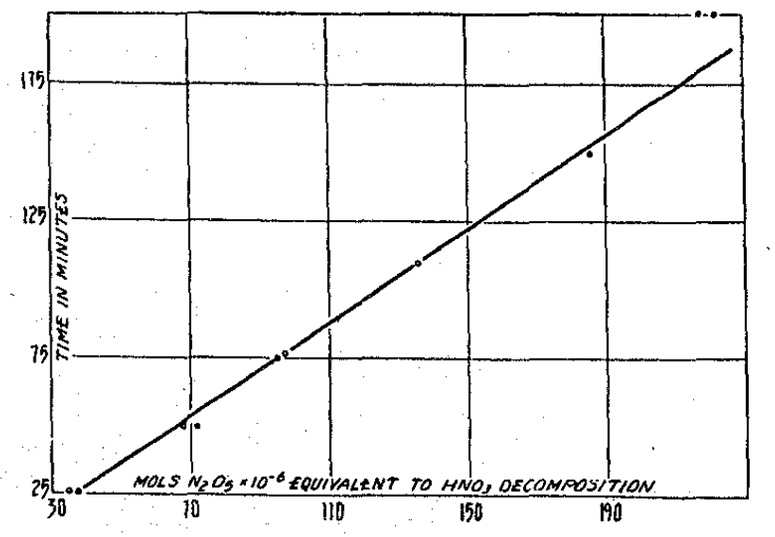
*Average total acidity determined by titration with standard alkali.

**Lueck's value = .00972. Daniels' and Johnston's value = .00808 (observed); .00790 (calculated).

Final results have not yet been obtained on the solutions of nitrogen pentoxide in nitric acid. Some preliminary experiments on the decomposition of nitric acid itself were carried out by heating the acid for twenty-five or thirty minutes at the temperature of boiling methyl alcohol. These were followed by trial runs on two different solutions of nitrogen pentoxide in nitric acid. The results pointed to a much slower reaction velocity than normal; in fact, less than one-tenth of the expected decomposition at 35°C. occurred. This suggested that experiments should be carried out at 65°C. for varying periods of time. Measurements were made on the decomposition occurring during intervals of from twenty-five to two hundred minutes. In the second solution which contained roughly 3% nitrogen pentoxide, the reaction velocity was calculated to be approximately .022 instead of the .286 of nitrogen pentoxide itself. During these runs the experimental method was being worked out, the temperature coefficient of the apparently different reaction is not known, also the concentration of nitrogen pentoxide was quite small which resulted in the decomposition due to nitric acid being a disproportionately large part of the total decomposition, consequently it is hardly possible to give any more definite quantitative data at present.

However, the figures on the decomposition of nitric acid are of interest. In the curve, shown on the graph in Fig. 1, the triangles represent the decomposition of approximately 99.7% nitric acid at 64.9°C., and the circles that of nitric acid which was probably very nearly the same concentration and at temperatures ranging between 64.4 and 64.6°C.

No explanation of the apparently increased stability of nitrogen pentoxide in nitric acid has been tested as yet, but the possibility of compound formation[1] between the two might be suggested and should be investigated by means of a freezing-point composition diagram.



Summary

1. No evidence has been obtained pointing to the decomposition of nitrogen pentoxide being a dust reaction. Apparently there is no catalyst for the reaction connected with the use of phosphorus pentoxide in the preparation and drying of nitrogen pentoxide, since the velocity constants remained the same when phosphorus pentoxide was obtained from different sources or was dispensed with altogether.

2. If nitric acid is a catalyst for the reaction, we have not yet been able to demonstrate it. In the course of attempts to do so, we have found that nitrogen pentoxide appears to be much more stable in 100% nitric acid than in the gas phase or in solution in organic solvents. Possibly this is due to formation of some compound.

3. It is of interest to note that Lueck's figures on the decomposition of the pentoxide in carbon tetrachloride solution have been confirmed by a simple and entirely different experimental method.

Baltimore, Md.

[1] Weber: J. prakt. Chem., **114**, 342 (1873); Veley and Manley: Proc. Roy. Soc., **69**, 86 (1901); Veley: Trans. Faraday Soc., **7**, 229 (1911).

ON THE CONTRACTION OF MOLECULES IN THE LIQUID STATE

BY SERGIUS G. MOKRUSHIN

According to the van der Waals equation,[1] the molecules of a liquid exist under very high pressure (up to ten thousand atmospheres or even higher) and we should therefore expect that the molecules of gas would undergo a contraction on passing into the liquid state. This hypothesis was put forward many years ago by T. W. Richards,[2] who has applied it not only to change of state but also to chemical reactions.

In this article the writer makes the two following assumptions in order to calculate this contraction.

1. In the state of vapour or gas the molecules are spherical.

2. In the liquid state they have the shape of the hexahedral prism of maximum volume that can be inscribed in a sphere. From this form the liquid molecule can further pass over into that of the honey-comb cell[3]—this latter having the same volume as the hexahedral prism but a smaller surface area.

On the basis of these assumptions the ratio of the volumes of the molecule in the gaseous and liquid states can be calculated as follows.

Let R = radius of a sphere

r = edge of an inscribed hexahedral prism

& v = volume of the prism.

Then $v = 3\sqrt{3}\, r^2 \sqrt{R^2 - r^2}$

Differentiating, we obtain as the condition for maximum value of v

$$r = R\sqrt{\tfrac{2}{3}} \qquad (2)$$

Substitute this value for r in equation (1), and divide through by the volume of the sphere $= v_1 = \frac{4}{3}\pi R^3$

$$\text{Then } \frac{v}{v_1} = \frac{2}{4\pi/3} = .47$$

In this expression v is now the maximum volume of the inscribed prism, and we have here therefore a measure of the contraction of the molecule in passing from the gaseous to the liquid state.

Of the two assumptions on which this calculation was based, the first follows at once if Langmuir's view[4] is correct, that each molecule possesses a surface energy by virtue of which its surface tends to a minimum. Such an idea is in fact made the basis of a structural theory of molecules by W

[1] Van der Waals: "Die Kontinuität des gasförmigen und flüssigen Zustandes," (1889).

[2] T. W. Richards: J. Am. Chem. Soc., **46**, 1419 (1924); **47**, 731 (1925).

[3] Arw. Fuhrmann: "Anwendungen der Infinitesimalrechnung in den Naturwissenschaften." Teil 1, 175 (1900).

[4] Langmuir: Colloid Symposium Monograph, **3**, 48 (1925).

Taylor[1] and by the founder of the kinetic theory. With regard to the second assumption on the other hand, there is little agreement concerning the form of the liquid molecules; van Urk[2] suggests a cubical packing, and Hildebrand[3] a close hexahedral packing. The author's view that a honey-comb structure is most probable, is borne out by the fact that soap bubbles formed in a closed space assume such a structure in accordance with the principle of minimum surface area.[4]

Further justification is afforded for this second assumption on the basis of Ramsay and Shields' modification of the Eötvös equation,[5] together with an equation deduced by the writer in earlier papers.[6]

These equations are as follows:—

$$\gamma S = J(Q - RT) = J\lambda_i \quad \ldots\ldots (3) \text{ (Mokrushin)}$$

$$\text{and } \gamma V^{\frac{2}{3}} = K(T_k - T - 6) \quad \ldots\ldots (4) \text{ (Ramsay \& Shields)}$$

where S = total surface of vapour molecules

Q = total heat of evaporation

and λ_i = internal heat of evaporation.

$$\text{Dividing (3) by (4)} \quad \frac{S}{V^{\frac{2}{3}}} = \frac{J}{K} \frac{\lambda_i}{(T_k - T - 6)} \quad \ldots\ldots (5)$$

If further v = volume of one liquid molecule

v_1 = volume of one vapour molecule

r_1 = radius " " " "

m = mass of one molecule

and d = density of the liquid

$$S = 4\pi r_1^2 N \text{ and } v^1 = \frac{4}{3}\pi r_1^3$$

$$\text{i.e. } S = 4\pi \left(\frac{3v_1}{4\pi}\right)^{\frac{2}{3}} N \quad \ldots\ldots (6)$$

$$\text{Also } V^{\frac{2}{3}} = \left(N\frac{m}{d}\right)^{\frac{2}{3}} = N^{\frac{2}{3}} v^{\frac{2}{3}} \quad \ldots\ldots (7)$$

Dividing (6) by (7) and comparing with (5) we find that

$$\frac{S}{V^{\frac{2}{3}}} = \frac{4\pi\left(\frac{3v_1}{4\pi}\right)^{\frac{2}{3}} N}{N^{\frac{2}{3}} v^{\frac{2}{3}}} = \frac{J}{K} \frac{\lambda_i}{(T_k - T - 6)} \quad \ldots\ldots (8)$$

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[1] W. Taylor: Ann. Phys. (10) **1**, 137 (1924); Phil. Mag., (6) **41**, 877 (1921).

[2] A. Th. van Urk: Verslag. Akad. Wetenschappen Amsterdam, **34**, 351 (1925).

[3] Hildebrand: "Solubility," Am. Chem. Soc. Monographs, No. 17, 112 (1924).

[4] Arw. Fuhrmann: Loc. cit.

[5] Eötvös: Ann. Physik, **27**, 448 (1885); Ramsay and Shields: J. Chem. Soc., **63**, 1089 (1893).

[6] S. Mokrushin: Phil. Mag., **48**, 765 (1924); Z. allg. anorg. Chem., **153**, 273 (1926).

Rearranging and evaluating known terms we obtain the ratio

$$\frac{v}{v_1} = \left(\frac{36\pi N K^3}{J^3}\right)^{\frac{1}{2}}\left(\frac{T_k - T - 6}{\lambda_i}\right)^{\frac{3}{2}}$$

$$= 112{\cdot}45\left(\frac{T_k - T - 6}{\lambda_i}\right)^{\frac{3}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

Now the value of $\left(\frac{T_k - T - 6}{\lambda_i}\right)$ can be determined at the boiling point (T_s), for by Trouton's Rule $\lambda_i = 19T_s$, and according to Guldberg and Waage $T_s = {\cdot}67T_k$

$$\frac{v}{v_i} = 112{\cdot}45\left(\frac{1{\cdot}56T_s - T_s - 6}{19T_s}\right)^{3/2} = 112{\cdot}45\left(\frac{{\cdot}56}{19} - \frac{6}{19T_s}\right)^{\frac{3}{2}}$$

$$= 112{\cdot}45\left(\frac{{\cdot}56}{19}\right)^{\frac{3}{2}} \text{ to a first approximation}$$

$$= {\cdot}57$$

Further evidence is thus afforded that the molecules are contracted in the liquid state. Comparing this value, however, with the one obtained previously for the maximum contraction, it appears that at the boiling point the honey-comb structure has not yet been assumed.

Summary

It has been shown that the molecules contracts on passing from the gaseous to the liquid state, and that a change in shape is suggested from that of a sphere, first to that of a hexahedral prism, and finally to that of a honey-comb cell.

The General Chemistry Laboratory
Polytechnic Institute of Ural
Sverdlosk, Russia.
April 7, 1927.

SOCIÉTÉ DE CHIMIE INDUSTRIELLE
28, Rue St-Dominique
PARIS
(7e)

NEW BOOKS

Elementary Physical Chemistry. *By Hugh S. Taylor. 22 × 15 cm; pp. ix + 531. New York: D. Van Nostrand Company, 1927. Price $3.75.* In the preface the author says: "The present volume attempts the presentation of material suitable for an introductory course in modern physical chemistry. It is adapted from the two-volume 'Treatise of Physical Chemistry' which appeared under the author's editorship some three years ago. A need has been felt in several quarters for a single volume of a more elementary nature which should follow the general lines of development in the larger treatise, without, however, its detail. This book is offered in response to such a demand.

"Anyone who has examined the scope of modern general chemistry cannot but be struck with the very considerable amount of physical chemistry which finds its place in such a course, often to the detriment of the purely inorganic chemistry. The physical chemistry is of course largely descriptive but it is substantially similar in form of presentation to that given in introductory physical chemistry courses a decade or so ago. Physical chemistry ought to reap the advantages of that development and is therefore offered the possibility of substituting for the descriptive, qualitative course a more rigorous and, therefore, more mathematical discipline. In the present case, it has been decided to take advantage of this state of affairs and to presume in this outline of physical chemistry a knowledge of mathematics which can be obtained in a course covering the elements of the differential and integral calculus. Another and more compelling reason for this decision, however, is the modern trend in physical chemistry. Any teacher who would advise his students that he can attain to an understanding of the science as now developing without the mathematical knowledge required in the present volume is, in the opinion of the author, doing an ill service to his pupils. If one needs conviction on this point let him turn to the current issue of the Journal of the American Chemical Society and find how many of the articles in the section of General and Physical Chemistry, for example, in the March issue, can be read intelligently without such mathematical ability."

The chapters are entitled: the atomic concept of matter; energy in chemical systems; the gaseous state; the liquid state; the crystalline state; the velocity and mechanism of gaseous reactions; the direction of chemical change; solutions; homogeneous equilibria; heterogeneous equilibria; electrical conductance and ionisation; weak electrolytes; strong electrolytes; photochemistry; colloid chemistry.

This book came as a disappointment and a shock to the reviewer: a disappointment because it was not better; a shock because it may be better than the reviewer thinks it is. The treatment seems to the reviewer to be distinctly formal and essentially superficial. If this presentation means real progress, the reviewer is very much of a back number—which may very well be true. There is no alternative, because there is no possibility of reconciling the author's general point of view with that of the reviewer. It may be that both will go under; but both cannot survive. There is nothing personal in this. The author's point of view is, unfortunately, that of the majority of physical chemists and illustrates the demoralizing effect of the theory of activity, as at present expounded. The question at issue is whether we are going to study concentrated solutions and to develop an exact theory, or whether we are going to stick to ultra-dilute solutions and to play with an approximation theory? Do we believe in one hundred percent dissociation of all electrolytes in all aqueous solutions, or don't we, and why?

A few specific illustrations will make the situation clearer. On p. 214, the author starts the discussion of the lowering of the partial pressure of a solution by deducing Henry's law. So far as we know, Henry's law is specific, depending on the nature of the solvent and of the solute. By an ingenious transformation with the aid of ideal solutions, the proportionality factor is made to disappear and the author comes out triumphantly with the so-called Raoult Equation ($p_o - p/p_o = x = N/(N_o + N)$), "where x will be the mol fraction of the solute present in the solution. The term N, refers to the mols of solute present, having

the molecular weight of the solute in the solution, while N_o is the number of moles of solvent present having the molecular weight of the solvent in the vapor state." There is of course no proof of this and the author has forgotten that this formula is only supposed to hold for ideal solutions, in which, by definition, the molecular weights of both components are constant throughout and the molecular weight of each is the same in the solution and in the vapor.

On p. 243 the author deduces the equation for osmotic pressure on the assumption that Henry's law holds, which is certainly not exact thermodynamics, unless we mean by exact thermodynamics a calculating machine to which the accuracy of the premises and of the conclusions is immaterial. The reviewer has not been able to find the fairly exact formula for osmotic pressure $PV_g = (RT/M)\log(p/p')$ where V_g is the volume occupied by one gram of the solvent and M is the molecular weight of the vapor of the solvent. He says definitely on p. 250 that, in the equation $PV = RT$, V is the volume of solution in which one mol of solute is contained. That has been known for years not to be true. On p. 253 we read: "It was found in the early work on direct measurements of osmotic pressure that results more concordant with experiment are obtained if instead of expressing *V* in terms of the volume of solution we express it in terms of the volume of solvent (water) at its maximum density. This variation really amounts to correcting for the volume occupied by the dissolved substance, analogously to the correction made in the case of gaseous pressures for the volume occupied by the molecules themselves."

As a matter of fact there is no justification for expressing V generally in terms of the volume of solvent (water) at its maximum density. It is quite debatable whether "this variation really amounts to correcting for the volume occupies by the dissolved substance." There is a very important theoretical point involved.

Variations from the gas laws are considered to occur when the concentration exceeds 0.2 molar, p. 221; but this is true only in case we postulate that sugar and water is our standard. With boric acid and boiling water the gas laws hold up to saturation, which suggests that the abnormal behavior of sugar solutions may be due to some other cause. On p. 209 the author points out very properly that liquid water is "an equilibrium of the molecular species H_2O, $(H_2O)_2$, $(H_2O)_3$, and perhaps others"; but the author does not point out anywhere, so far as the reviewer has seen, that any change in the water equilibrium must affect the application of all laws deduced on the assumption that the water equilibrium is not displaced. Perhaps the author believes that the rapid rate at which equilibrium is reached precludes the displacement of equilibrium; but that seems impossible. No reference is made to this possibility when discussing the effect of sodium chloride on the inversion of sugar by hydrochloric acid and there is not even a reference to the impossible apparent concentrations of hydrogen ion obtained under these circumstances. We account for the abnormal maximum density of water by postulating different densities for the different modifications of water. We account for the abnormal boiling-point of water on the basis of a difference in the properties of the different modifications. We account for the abnormal surface tensions of water by a change in the water equilibrium. We know that the color of NO_2 is not identical with the color of N_2O_4. We know that the properties of acetone are not identical with those of diacetone and we know that the properties of S_λ are not identical with those of S_μ, and yet the author does not consider it worth while even to mention that displacement of the water equilbrium might have an influence in some cases.

The author mentions, p. 257, the work of S. U. Pickering, "who found that if a solution of propyl alcohol and water in a porous cup be surrounded by either the pure alcohol or pure water, there is always an osmosis of the pure liquid into the cup. This would indicate that the porous cup is not impermeable to any one constituent of the solution but rather to the hydrate formed in solution." Pickering never showed that the cup was impermeable to the alleged hydrate. All he showed was that the initial flow was predominantly from either pure liquid to the solution in case the solution has a suitable composition. Given time enough and the concentrations on the inside and the outside of the cup would be the same.

The author does not say definitely that complete ionization in a crystal connotes complete ionization in aqueous solution; but he implies it, p. 428. "The most recent efforts to explain the deviations from the law of the mass action shown by strong electrolytes have centered around the idea that the theory of partial dissociation is incorrect. A number of lines of evidence have contributed to this idea. By no means the least important evidence came from an entirely unexpected quarter, the analysis of solid salt crystals by the X-ray method of analysis. According to Debye, the intensity of a beam of X-rays reflected from atoms depends upon the number of electrons in the outer shell of these atoms. Upon this basis, in a crystal of sodium fluoride, the intensities should be equal if the lattice points are occupied by ions and unequal if there are atoms present at such points. The experimental evidence was in favor of ions. Further considerations confirm this view. It is possible, on the assumptions that ions are present, to calculate the work involved in separating these ions to infinite distance from each other. This energy quantity is known as the lattice energy. The values obtained in such calculations can be used to determine magnitudes which are experimentally verifiable. The agreement obtained between experiment and calculation constitutes a confirmation of the concept of an ion lattice in such solid salts. It was also shown by the physicist, Rubens, that such solid salts as potassium chloride, when utilized as reflectors for infra-red radiation, selectively reflect light of wave-lengths characteristic of the vibrations of the constituents of the solid salt. These residual rays could only be produced if the vibrators were ions."

"If, therefore, in the solid state, such substances as potassium chloride are wholly ionic, it may be assumed that in solution, with the ions separated by solvent molecules, complete dissociation is probable," p. 429. If this were a necessary consequence, as many people seem to think, it would apply to all solvents, which nobody has yet been willing to advocate. Thirty-six years ago Nernst pointed out that a high dissociating power for a liquid was equivalent to a high solubility coefficient for the ions. The converse is also true. Complete dissociation at all concentrations for potassium chloride means that the molecule of potassium chloride, which can exist as vapor, is absolutely insoluble in liquid water. When discussing Henry's law, Taylor says, p. 290, that "Nernst shows that we cannot logically think of a substance as distributed between two phases if its molecular condition in the two phases is different." Assuming this statement to be true, it follows that hydrochloric acid which exists as a molecule in vapor must therefore exist to some extent in the undissociated form in water. This amount may be very small; but if there can be some, there is no theoretical reason why there should not be more.

Nernst's approximation formula for concentration cells is referred to, p. 439; but the reviewer has found no reference to the exact theory of Helmholtz. Incidentally, the author mis-spells cation and cathode, and also Grotthuss.

The Grotthuss-Draper law is given, p. 473, in the perfectly proper form that "only the rays that are absorbed are effective in producing chemical change;" but there is no reference to the further work of Grotthuss on photochemical depolarizers. Instead, we have the perfectly true but not very helpful statement that "not all absorbed radiation results in chemical change. The numerous investigations of spectroscopy demonstrate the occurrence of absorption of light in many cases entirely unassociated with chemical change. In such case, the light suffers a transformation into one or other forms of radiant energy or into change in the energy content of the molecules, which change, however, need not result in chemical reaction. Photochemical change is, therefore, one possible resultant of the absorption of radiation. Furthermore, as will be more fully discussed in the sections dealing with photosensitization, it is not necessary that the reacting species absorb the radiation. Photo-reactions may result from the absorption of light by one of the non-reactive constituents of the system."

At the meeting of the National Colloid Symposium held at the University of Michigan last June, the reviewer felt, and said, that the European view-point, as exemplified by Kruyt, was five to ten years behind that in America. After reading the pages on lyophile colloid solutions, pp. 517-518, the reviewer feels almost like apologizing to Mr. Kruyt.

Changing to a less important point, that of order, it seems a pity to take up reaction velocity before equilibrium relations. In his capacity as a possible back number the reviewer still holds to what he wrote thirty years ago about Ostwald's great text-book. "At first sight it seems natural to begin with the approaches to equilibrium and then to study the phenomena of equlibrium. Guldberg and Waage started from the kinetic theory of gases and deduced an expression for the velocity of reaction. According to this view there could be equilibrium only when the rate of formation of one system was equal to the rate of decompositon of the same system, and it was therefore natural to broach the subject of chemical affinity by a discussion of velocities. On the other hand we do begin our studies of chemistry, either as individuals or as a race, by examining cases of equilibrium. Most chemists never get beyond a study of qualitative equilibrium and the physical chemist passes in the laboratory from qualitative to quantitative equilibrium and then to a study of the laws describing the phenomena of change. There seems to be no good reason why the teaching of the text-book should reverse the teaching of the laboratory. It is urged by some that we must consider equilibrium as a dynamic phenomenon, involving the balancing of two velocities; but this is not true. There is no balancing of velocities when a voltaic cell is opposed by an electromotive force equal to its own, and yet there is equilibrium. This conception is a relic of the kinetic theory of gases and it is surpsising to find Ostwald, of all people, adopting it. For our purposes, it is better to start from the theorem of Wenzel, 1777, quoted by Ostwald, p. 40, that the strength of the chemical action is proportional to the concentration of the reacting substances. That is the most general and the most accurate statement of the mass law which can be made today."

Gibbs did not deduce his criteria of equilibria from a balancing of reaction velocities. The decisive point, so far as the reviewer is concerned, is that we can deduce the form of the equilibrium equation without a knowledge of the intermediate stages, whereas the form of the reaction velocity equation depends entirely on the question whether there are or are not intermediate reactions and on the relative speeds of these intermediate reactions.

The author is enthusiastic over the theory of activity. When discussing the electromotive forces of amalgam concentration cells, p. 439, he says that "it is apparent; from a comparison between the calculated and experimental results, that, at low concentrations of amalgam, the agreement is fair, but that, in the more concentrated solutions, there is a very great discrepancy between experiment and the requirements of theory based on the laws of ideal solutions. It is evident therefore that for a general treatment of solutions some alternative method of theoretical approach is required. This need has been met in the use of the *activity function* introduced into thermodynamic chemistry by G. N. Lewis." There is not a word to show that there are any objections to this theory, which means that no criticisms have been made which seem to the author worth mentioning. Evidently, the walls of Jericho did not fall down at the first blast of the trumpet.

"The incompatibility between the postulates of Arrhenius concerning the degree of dissociation of strong electrolytes and the evidence for complete ionization of such electrolytes have led to a number of efforts which, starting from the assumption of complete ionization, would obtain expressions in agreement with the results of experimental measurement of the thermodynamic properties of such solutions. Of these efforts the most notably successful is that of Debye and Hückel. These authors assume that, in dilute solution, the departure from validity of the laws of dilute solutions found with strong electrolytes, is to be ascribed to the ionization. They point out that, in a solution of a non-electrolyte, the relation between the partial free energy and the concentration is given by the expression

$$F = RT \ln c + \text{Const.}$$

They suggest that, for a solution of an electrolyte, the free energy is given by the expression

$$F = RT \ln c \, \bar{F}_e + \text{Const.},$$

where, in addition to the terms normally obtained with a non-electrolyte, there is an additional term, $\bar{F}_e$, associated with the electrical free energy, the energy effect due to electrical forces between the ions. These forces act in such a way that in the neighborhood of any ion, there will be more ions of unlike sign than of like sign. Consequently, a

dilution of the solution involves, in the separation of the ions, an amount of work done against this electrical attraction and, therefore, a corresponding increase in the energy content of the solution," p. 445.

What Debye and Hückel have done is to assume that the formula with which they started was absolutely accurate except for disturbances due to the electrical changes of the ions. They have then adjusted their assumptions perfectly frankly so as to make their calculations agree with the facts. There is no possible objection to this; but agreement between the observed and the calculated results does not prove the accuracy of the assumptions any more than it did in Loeb's work on the proteins. If we have an effect due to an ion which is not a function solely of its electrical charge, this introduces another term and the calculations must be revised because the agreement between the observed and the calculated data is then fictitious. Similarly any error in the original formula vitiates all that follows. This is not the place to discuss the validity of the thermodynamical formulas from which Debye and Hückel start, though the reviewer has very definite opinions on this point. It seems to the reviewer, however, that the existence of a Hofmeister series in true solution is satisfactory evidence of the existence of a specific factor which is a function of the nature of the ion and not solely of its electrical charge. If, for instance, iodine ion displaces the water equilibrium differently from chlorine ion, all the calculations of Debye and Hückel will have to be revised. This does not mean that their work goes into the discard. Nobody questions the possibility or the probability of disturbances due to electrical charges. The whole question is whether one hundred percent or less of the variations is due to this cause.

It would be an excellent thing if the physical chemists of the world would get together in a co-operative effort to develop a satisfactory theory of concentrated solutions, perhaps under the auspices of the National Research Council; but that time seems still far distant. It is to be hoped, however, that the tide has turned and that this book represents high-water mark for the theory of activity which has threatened to engulf us.

Wilder D. Bancroft

Kinetic Theory of Gases. *By Leonard B. Loeb. 23 × 16 cm; pp. xvi + 555. New York: McGraw-Hill Book Company, 1927. Price: $5.50.* In the preface the author says: "The last thirty years have seen the beginning and development of a new period in physics and chemistry, namely the atomic period. In contrast to the period preceding it where nature's processes were described in terms of continua, recent developments have emphasized the discrete structure of the submicroscopic universe. Thus, today one hears of the atoms of matter, the atoms of electricity, and even the atoms of energy, the quanta. Accordingly the modern physical sciences are demanding and constantly using atomic terminology, concepts, and methods of analysis. It is therefore important that the physicist and chemist have available a fairly complete understanding of these methods.

"Of all atomic concepts, the atomic theory of matter is the oldest and perhaps the most complete. In particular because of its relative simplicity the problem of the atomic nature of gases, in the form of the kinetic theory of gases has attained the highest degree of perfection in this field. Its admirable methods of analysis are therefore indispensable not only for prospective physicists, but for both chemists and physicists engaged in experimental or teaching work.

"When attempting to teach a course on the kinetic theory of gases, at the University of Chicago, in the summer of 1922, the writer discovered that there was in print but one text in the English language on modern kinetic theory. This text was far beyond the scope of the average American college student including even the first-year graduate students. The lack of facility in foreign languages among the students precluded references to texts in foreign languages. Finally, in his own field of work, which depends on the kinetic theory, the writer and his students have been much hampered by lack of a handy reference book containing a collection of the classical and more moden aspects of the kinetic theory. This book was written in an attempt to meet this situation."

The chapters are entitled: historical; the mechanical picture of a perfect gas; the mean free path; the distribution of molecular velocities; the more accurate equation of state, or

van der Waals' equation; transfer of momentum, of energy, and of mass through a gas; the laws of rarefied gases and surface phenomena; the reality of molecular motions; specific heats and kinetic theory; contributions of kinetic theory to electrical and magnetic properties of molecules; application of the kinetic theory to the conductivity of electricity in gases.

If "a" is the constant of an equation giving the number of electrons which escape molecular encounters in going x cm in the gas, "it is seen that in order of magnitude the values of "a" at the higher speeds are nearly the same as those for "a" computed from kinetic theory. For still higher speeds, "a" decreases rapidly as the velocity increases. This is easily explained, since it is only for lower speeds that the collisions of electrons with molecules are elastic and they are deflected by the surfaces of the molecules. At higher speeds the electrons begin to shoot through the molecules. The behavior at the lower velocities is nearly normal for all but the inert gases. At speeds near those exciting characteristic resonance effects in the electrons of the atoms or molecules themselves, the bombarding electrons, especially in the inert gases, seem to be much more readily deflected than otherwise. Thus the effective ares of the molecules are increased and the mean free paths fall to lower values. At still lower speeds the atoms of argon, neon, krypton, and xenon appear to become more transparent to electrons than the kinetic theory demands. In fact, the area for argon drops to one-fifteenth its kinetic-theory value at the lowest velocities, or the mean free path is multiplied by about 15. The meaning of this is obscure, and is characteristic of the peculiar symmetry of the inert gas atoms. The other gases appear to show nearly normal free paths as the velocity decreases.

"On the whole, then, the electron free paths lead to a brilliant confirmation of the distribution law and agree surprisingly well in magnitude with those computed from molecular free paths and the kinetic theory," p. 54.

"A theoretical study of the behavior of electron atmospheres has shown that these are in all respects analogous to gaseous atmospheres. They differ from them chiefly in the smaller masses of the electrons and their mutual repulsion due to their charges. For the great attenuation of the atmospheres in a number of experiments the distances between individual electrons becomes so great that the potential energy of the forces of repulsion are negligible compared with the kinetic energies possessed by the electrons at those temperatures. Thus the electrons sensibly obey the laws of a perfect gas, i.e., $pv = RT$, or $p = NkT$, where N is the number of electrons per cm^3, k is the gas constant per electron or per molecule, and T the absolute temperature. Hence it would not be surprising to find that in such an atmosphere the average kinetic energy of one electron is $3kT/2$ and that the energies are distributed according to the Maxwell distribution law.

"Now it was at one time believed that these electron atmospheres existed even in the interiors of metals, and that thus the electrons might be in thermal equilibrium with the atoms of the metal. Thus on heating a metal, if the Maxwell distribution law held inside the metal, electrons emitted because of their heat motions would, by Sec. 43, be expected to show this same distribution outside. This assumption, according to Richardson, may be applicable even if the electrons are emitted from the surface and flow away constantly without attaining a steady state. Whether the Maxwellian distribution exists in the dense electron atmospheres assumed inside the metal surfaces, or even whether such atmospheres exist at all (a point which is at present open to a reasonable doubt), the fact remains that Richardson has predicted that the electron streams emitted from the surfaces of incandescent metals have the energies corresponding to electrons in thermal equlibrium with the surface, and that their energies are distributed according to Maxwell's distribution law. Such a definite prediction deserves experimental test. If it is found to correspond to facts, then it is a fact of great importance whether the initial assumptions of Richardson (which he has in part modified) are correct or not, for no matter what the mechanism is, one would have definite proof that electrons emitted by a hot body are: (1) in temperature equilibrium with it according to the law of equipartition and of Maxwell, and (2) that the electrons have a distribution of velocities predicted by Maxwell's law. Thus one would have a directly measurable quantitative verification of a Maxwellian distribution of velocities existing in the heat motions of particles of matter. This point must be stressed, for except

for the two other proofs which are given in this chapter, both of which depend on the constants deducible from the Maxwell law, no direct verification of the distribution exists. Outside of these three experimental verifications, the distribution law is unproved experimentally, for it only appears in constants of the kinetic theory whose value is the subject of dispute owing to uncertainties in averaging. Thus the experimental verification of such constants up to the present furnishes no certain proof of the validity of the present law, and all available evidence is of value," p. 105.

"In a recent paper Jones has eliminated a number of the errors inherent in Schottky's work and succeeded in obtaining values of R which deviated less than 15 per cent from the true value of R between temperatures of 1450° and 2000°K. The deviations were nearly equally great on both sides of the true value and the average deviation was about ±5 per cent. Very recently the experiments of Jones were extended by Germer, using a straight tungsten filament and a cylindrical electrode. He also used a device for heating his filament and measuring the thermionic currents when the heating current was off. Measurements were made at eight different temperatures from 1440° to 2475°K. Correcting for the contact difference of potential between the filament and the grid, it was found that at each temperature (except at very low voltages where the space charge effect limited the current) the *current varied with the voltage in just the manner calculated on the assumption that the electrons leave the filament with velocity components distributed according to Maxwell's law for an electron atmosphere in temperature equilibrium with the hot filament.* At 2475°K the assumed *Maxwellian distribution was verified up to a retarding potential so great that only one electron in* 10^{10} *emitted electrons was able to reach the collector.* This accurate extension of the previous measurments verified the law over a large range of temperatures, and over a remarkable range of velocities. It constitutes probably the best quantitative verification of the law, in that it verifies it over so great a range of velocities. Thust the fact must be accepted that—no matter whether the theoretical assumptions are correct—(1) the electrons are emitted from a hot metal with the mean energy which the Maxwell distribution law would lead one to expect; and (2) the velocities are distributed among the electrons in accord with the Maxwellian law to within one per cent. Thus the Maxwellian law has been obtained and verified quite definitely in one case, *viz.*, that of the velocities of electrons which are purely of thermal origin," p. 110.

"It is of interest to note in passing that the development of Boyle's law is a beautiful illustration of the progressive advance of physical science. First there is the discovery of a general regularity or law of nature through crude quantitative measurement. This is followed by a stimulating "explanation" in terms of a mechanical analogy. Then, as the result of more accurate measurements, what might be called second-order deviations come to light. Following these appears a brilliant *extension* of the mechanical theory to include the deviations. It is to be noted that such a change in the theory is not *revolutionary* in any sense. Nothing is upset and no errors have been made. The further investigation merely indicates the limitations of the fundamental assumptions. Such limitations being discovered, a further extension is possible, and the accuracy of the theory is extended perhaps to another significant figure. Following this improvement still more precise measurement again reveals deficiencies which require extension of the theory. Thus the knowledge and comprehension of the phenomenon can continue indefinitely, new improvements in technique making further experiment possible, new extensions in mathematical treatment also making perfection of the theory possible. It might seem as if this process would go on *ad infinitum*. Unfortunately, as accuracy advances progress becomes increasingly difficult, owing to t he increase in mathematical complexity. Thus it soon becomes almost impossible to handle some of the resulting involved expressions. A simple example of this also appears in the practical application of the equation of state. To this day most engineers are, for simplicty, forced to assume the Boyle's law equation, since the complications introduced by the more accurate van der Waals' equation already begin to increase the complexity of their calculations more than the increase in accuracy would warrant.

"The van der Waals' equation, accordingly, besides furnishing an admirable second approximation to the true behavior of gases, can be of value in indicating the manner of ad-

vance of scientific thought. From what has preceded, it is seen that, while it has its limitations, it is perhaps the most serviceable equation, for, owing to its still considerable simplicity, it makes it possible to deduce the values of the constants involved (*e.g.*, the size of the molecules and the constant of attraction) to the first order of approximation. With the more accurate modifications the increasing complexity of the quantities render such evaluations more difficult, and the loss of generality in application renders correlation between the constants of the equation obtained from a variety of phenomena impossible. Thus by its means, as will be seen in this chaper, the molecular constants a and b can be determined and can be found to agree from three apparently independent sets of data, to wit: (1) deviation from the gas laws, (2) critical constants, (3) the Joule-Thomson effect," p. 121.

"Jellinek shows that each of the isotherms of Andrews can be fitted closely except in the unstable region) by van der Waals' equation if the proper constants are chosen. Good agreements can be obtained at the following temperatures for the values of a and b given:

Temperatures	$b = 0.0023$, curves fit for a	$a = 0.008497$ curves fit for b
6.5°C.	0.008497	0.0023
64.0°C.	0.007529	
100.0°C.	0.006798	0.0032

Thus the equation fits for either b constant and a varied, or a constant and b varied. From 6.5° to 100° the a values vary 20 per cent when b is constant, and for a constant the b values may vary by 30 to 40 per cent in this same range. Jellinek says that the use of a variable a seems more adequate for this reason as well as from the indications of the data on the variation of B, the pressure coefficient, with temperature. On the other hand, van der Waals' theory demands that b vary with the volumes when these become small and a might be expected to vary with volume also. So that variations in both a and b with volume and temperature are to expected, a varying less with volume than b and b less with temperature than a," p. 159.

"In studying the evaporation processes of metals from filaments, as well as certain chemical effects caused by them, Langmuir had arrived independently at a somewhat different view of such phenomena. He believed that for the cases observed by Wood of what the latter termed diffuse reflection, one had no reflection in the real sense, but an actual case of condensation and reevaporation. At first sight it might be thought that the distinction between a diffuse reflection and a condensation and reevaporation was rather a hair-splitting one, for in any cse the condensed layer of atoms postulated by Langmuir cannot be appreciable in thickness. Thus the atoms must condense and reevaporate very rapidly. In fact, it is conceivable that the time of impacts with the surface, resulting in diffuse reflection, is quite the same as the time which the condensed atoms spend on the surface. If this were true, the two processes would *appear* to be indistinguishable in the limit, and perhaps they are so. This is only an appearance in the general case and the difference in point of view is an important one near the critical temperature which can be tested experimentally. If reflection takes place at a given temperature, and if there is a critical temperature of condensation, the condensation may occur sharply at the critical temperature and *will not depend on the density of the stream of impinging atoms*. On the other hand, on Langmuir's condensation and reevaporation theory, condensation and evaporation will depend very markedly on the density of the atomic stream, for the rate of evaporation depends on the temperature, while the rate of condensation depends on the density of the atoms near the surface. For low stream densities where evaporation is rapid compared to condensation, the two phenomena may appear to be the same and in the limit may be so. Near the condensation temperature a considerable increase in the density of the stream of atoms could cause an accumulation of atoms on the surface which would disappear on reducing the stream density, provided a condensing layer did not fully form. No change would occur on reflection, for the number of reflected atoms would be equal to the number of the impinging ones. Long since Langmuir's article came out, Chariton and Semenow, by a very ingenious scheme, have actually shown that the condensation on a surface with a temperature gradient down

its length occurs at lower temperatures where the density of the atom stream is reduced. The evidence is not accurately quantitative and one may question it on other grounds. Until it is more definitely proved, it must not be accepted as final. It, however, points strongly to the correctness of Langmuir's point of view," p. 309.

"Langmuir studies the amount of reflection from surfaces by a study of the rate of chemical reactions. If one calculate from the rate of a surface catalysis the ratio of the number of molecules which react to the number of molecules striking the surface a fraction ϵ is obtained. He assumes that the molecules that react must stick. This $1 - \epsilon$ is the reflectivity, or at least the upper limit for it. The values of ϵ found in some reactions are interesting, but it would seem hardly convincing as regards reflectivity, for in a reaction of N_2 with CuO giving atomic nitrogen the value of $\epsilon = 0.002$ was found. This probably indicates that the reaction did not occur for every molecule which was not specularly reflected, for it is quite likely from slip measurements that ϵ for N_2 on CuO is as high as 98 per cent or even more, and not 0.002. Again, it is possible that the value of ϵ in a reaction may be very much higher than the value of a, the accommodation coefficient. This is the case for H_2 molecules striking a filament of tungsten at 2700°K. Here ϵ was 0.68, while at 1500°K. the value of a for H_2 was 0.19. This Langmuir attributes to the fact that at 1500°K. the filament is covered with H_2 molecules, while at 2700°K. it is clean and bare and thus reacts with H_2 molecules. Finally, this, in general, raises the question whether a reaction in which the chemical forces acting between a specific surface and a specific gas permits generalization about the nature of impacts between surfaces where this is not the case. All that these results show is that chemical forces of one sort or another between surface and gas can influence the nature of the "reflection" process. Unquestionably, all degrees of intensity of forces exist. It is not surprising, then, that there should *be all possible degrees of condensation occurring on surfaces and possibly even cases where reflection in a true sense occurs, as it must do where specular reflection is observed,*" p. 315.

"In view of what has gone before in the case of gases, it is a simple matter to explain the law of DuLong and Petit on the kinetic theory. In the solid state, and especially in crystals, it is assumed that the atoms or molecular groups are bound in fixed positions relative to each other. Thus there is not the motion associated with the solid state that characterizes the liquid and gaseous states. Heat motions, obviously, exist, for solid bodies both transmit and absorb heat. Thus they must be capable of taking up the kinetic energy from a gas and, in turn, passing on energy to a gas. A body held in a fixed position, while not free to execute random heat motions, may well move if disturbed. Such a motion will be an oscillation or a vibration about its rest position as center. Since it is likely that, within certain limits, the forces urging the displaced atom or molecule in a solid back to its initial position may be assumed to obey Hooke's law, the particles then exceute simple harmonic vibrations about their equilibrium positions. Thus the heat motions in a crystal consist of vibrations of the atom or molecules about their rest positions. Since on the average, each such degree of freedom of harmonic vibrations has equal amounts of kinetic and potential energies, there are 2 cal. per degree C associated with each degree of freedom of vibration in a gram-molecule of solid. As there are only three degrees of freedom of vibrations possible, along the three coordinate axes, the molecular heat should be

$$MC_p = 3 \times R = 6 \text{ cal. per degree C.}$$

Thus DuLong and Petit's law that each molecule or atom has associated with it a given amount of the absorbed energy which goes to raise its temperature at once finds its explanation in terms of the kinetic theory and the law of equipartition. With the exceptions discussed before, and which will be analyzed in what follows, this law holds for the elements very closely. For complex solids the law of Neumann holds. Here it is found that each molecule often does not absorb its full 6 cal., but where certain groupings appear the energy absorbed is less. This finds immediate and simple explanation in the view now held of the crystal structure in the case of complicated molecular groupings. Thus in $CaCO_3$ the crystal is built up of Ca atoms and CO_3 groups. The latter then act as a unit. It is quite plausible to assume that each of the atoms in this CO_3 unit are not free to vibrate in all

three of their degrees of freedom. Hence it is to be expected that where the CO_3 group occurs its contribution to the molecular heat may not be 24 units, but less, owing to some of the vibrational modes suppressed in its component atoms. Why some modes are suppressed and others not is explainable on the basis of the quantum theory, for if one of the oxygen atoms is very rigidly bound to the CO_2, and not equally so bound in the group along the three axes, it will require blows of greater energy to set the particular vibration into operation—that is to say, it is possible that at the existing temperature the average kinetic energy is too low to awaken the particular mode of vibration. Hence only those vibrations which are loosely enough bound to be active at the temperature in question should respond, and the energy absorption will be less by 2 cal. for each such "sleeping" degree of freedom. Of course, since the energy exchanges are statistical, an occasional degree that is normally "sleeping" will absorb. More of these will absorb the higher the temperature. Thus the molecular heat of such a compound will begin to go up as certain temperatures are approached. This increase will at first be gradual and then more rapid, but in any case more or less continual, due to the continuous value of the energy distribution function," p. 375.

"The verdict of this evidence [from the specific heats of solids] on the whole, seems to be that *in no metal are there numbers of 'free' electrons closely comparable in number with the atoms of the metal.* At higher temperatures the electrons certainly partake of the energy of agitation. Thus it would seem that the specific heat data answer the question of the old 'free electron' atmosphere quite decisively, while they also indicate the presence of electrons very loosely found," p. 379.

"The recent work of Lennard Jones, based on the study of gases, gives the repulsive forces as lying between an inverse ninth power and an inverse fifteenth power, while the attractive forces lie between forces varying inversely as the fourth power and inversely as the sixth power. With atoms and molecules of such a nature, the meaning of the term 'diameter' must be modified or at least one must understand the application of the term to such a picture. Measurements of molecular diameters are made in all cases on a *very large number of individuals.* In all cases for gases they are made for *individuals oriented in all possible directions.* Finally, in the case of gases, the conditions of impact due to velocity distribution will influence the distance of approach; and one must deal with an *average value.* It is *possible, therefore, to couch the experimental conclusions in terms of the very simple picture of elastic spheres of a given diameter, the diameter in such a case being the statistical average distance of approach of the molecules for the average velocity.* An analysis expressed in terms of such a picture is entirely justified, as it influences the results but little, while it simplifies calculation and interpretation greatly. When such pictures are used, however, one must remember that they are conveniences and that the actual molecules may be entirely different in appearance. Even in the case of crystal analysis, the investigators find it convenient to express atomic diameters in terms of the elastic sphere," p. 253.

Wilder D. Bancroft

Physico-chemical Metamorphosis and Some Problems in Piezo-chemistry. *By Ernst Cohen. 23 × 15 cm; pp. 190. New York: McGraw-Hill Book Company, 1926. Price: $2.50.* In 1925 Mr. George F. Baker endowed a non-resident lectureship in chemistry at Cornell University. This means that each half-year the students will hear a course of lectures by some distinguished man either in chemistry or in allied fields of science. Professor Cohen was the first of these lecturers, Professor Paneth the seond, and Professor A. V. Hill the third. This volume contains Cohen's lectures. It is a part of the programme that each lecturer shall publish a similar volume.

The ground to be covered is a matter for the lecturer to decide, which means that he will usually discuss the subjects on which he himself has worked. The title of this volume shows that this is what Cohen has done. In the lectures on physico-chemical metamorphosis, we are told about the tin disease, explosive antimony, inversion cells, cadmium iodide, thallous picrate, ammonium nitrate, etc.

"If a warm, saturated solution of thallous picrate be cooled below the transition temperature of the salt—you will remember that the red form changes to the yellow at 44°C.—both forms will crystallize out simultaneously and will remain in their respective states for several months even in contact with the solution. If the water be allowed to evaporate, a *mixture* of both modifications is obtained despite the fact that they are in intimate contact with each other. Such mixtures we have preserved for more than five years at 15°C., some 25 degrees below the transition temperature," p. 80.

"Summing up what has been said in these lectures it may be stated that most, if not all, hitherto determined physico-chemical constants of solid substances are in need of a revision, since it is very probable that the present values refer not to the physically and chemically pure modifications, but to physically impure and metastable mixtures which contain the respective forms in unknown proportions. This state of affairs opens up an immense field of research to scientists and investigators, and one which may yet have many a surprise in store for us. In the limited time at my disposal I have been able to give you only a brief outline of this interesting subject, but it is nevertheless one which presents an entirely new prospective to science," p. 94.

In the lectures on piezochemistry, Cohen described his apparatus and then discussed the influence of pressure upon reaction velocity, solubility, electromotive force, Faraday's law, rate of diffusion, etc.

In regard to Faraday's law, Cohen decides, p. 144, that "taking all things into consideration it may be said that the charge of an ion most probably does not change up to 1500 atmospheres, at least not to an extent greater than 1 part in 17000. Attempts have also been made to determine whether or not the transport number of a cation or an anion changes with external pressure. These experiments have been unsuccessful to date, so that the solution of this problem must be relegated to the future."

The reviewer is not enthusiastic over the author's use of the word *Bodenkörper* instead of solid phase or over the term "fictitious solubility," which is a bad translation from the German.

The non-resident lectureship is a very valuable asset to the University; but there are problems in connection with it which have not been solved and which will confront other universities when they adopt some similar practice. The lectures are given primarily to seniors and graduates in chemistry. A number of the seniors will not be planning to specialize in physical chemistry, for instance, and consequently the lectures must be more elementary than if the lecturer were speaking to a more homogeneous group. That is inevitable; but, either owing to this cause or some other, there has been a tendency on the part of all three lecturers to spread the lectures pretty thin—more so than was absolutely necessary. There is another problem which has not been faced and that is the form of publication. It seems to the reviewer that it would be desirable to have the published form differ more from the spoken one than it now does. The lecturer could then write up his work for the benefit of a more specialized audience, which would be more interesting both to him and to them. If it were not necessary to publish everything that was said, the lecturer could let himself go more and could talk more about his guesses and his hopes, which would be more interesting to the audience.

Wilder D. Bancroft

History of the Sciences in Greco-Roman Antiquity. *By Arnold Reymond. Translated by Ruth Gheury de Bray. 19 × 13 cm; pp. x + 245. New York: E. P. Dutton and Company, Price: $2.50.* There is a preliminary chapter on science in Egypt and Chaldea and the rest of the book is devoted to Greek and Roman Science. Under the general heading of historical outline the special chapters are entitled: the Hellenic period; the Alexandrian period; the Greco-Roman period. Under principles and methods are four chapters: the mathematical sciences; astronomy; mechanics and physics; the chemical and natural sciences.

"In connection with the annual risings of the Nile, the Egyptians attached great importance to the exact determination of the periodic return of the seasons, and the religious festivals held in its celebration; and their observations relating to the measurement of time

were far advanced. As far back as we go in the history of Egypt, we see that the year was always divided into 12 months of 30 days each, plus 5 supplementary days; but it is probable that originally the year had only 360 days," p. 9.

"Having noted the succession of eclipses which were produced during the cycle, it was possible for them to predict their return. It is probable, however, that a calculation of this kind does not belong to a period earlier than the second or third century B. C., and that, before that epoch, the Babylonians were ignorant of the so-called cycle of Saros. At first the prediction of the eclipses of the moon could be made by very simple methods, thanks to especially favourable circumstances, which return periodically in the course of centuries. From 755 to 432 B. C. the eclipses succeeded one another in series alternately of 5 and 6. In each series the eclipses took place every six months, and the series were separated by an interval of 17 lunations. Thus it became possible to make predictions at short notice, which explains some of the inscriptions found on the cuneiform tablets," p. 11.

"If the conquests of Alexander the Great caused Greek language and Science to penetrate into the East, they also brought about an upheaval of existing conditions. Greece lost her creative originality at the same time as her political autonomy. Athens certainly remained the seat of the philosophical schools, but in reality other towns, foremost amongst them Alexandria, became the centers of intellectual life. This now changed its character; instead of, as in the past, spreading through small democratic states, it concentrated in the capitals of the kingdoms which arose on the ruins of Alexander's empire, and hence was confined to smaller and smaller circles, for in spite of its diffusion, the Greek language, with its characteristic syntax and vocabulary, remained an unknown tongue to the masses of Asia Minor and Egypt. The classical works of Greece could only be appreciated by the chosen few. This state of affairs was unfavourable for literary and philosophical production. The latter, when it is intended for only a small circle of readers, is no longer animated by popular inspiration, and loses itself in sublety, affectation and erudition. But for the sciences properly so called, these conditions were very advantageous. Owing to the diffusion of Greek culture throughout the eastern littoral of the Mediterranean, specialists were sure to meet with savants capable of understanding them: thanks to the munificence of princes, had at their disposal the necessary resources for their work, and the wise administration of the kingdom secured to them the peace of mind needful for their meditations. Such peace and material independence could not be offered by the little democratic states of Greece, always a prey to revolutions.

"The Ptolemaic dynasty is especially noteworthy for its intelligent initiative in establishing Alexandria as the new and indisputable centre of Hellenic culture. The founder of this dynasty summoned to him Demetrius of Phalerus and Strato of Lampsacus, both representatives of science and the Aristotelian tradition, but it was his son Ptolemy II (Philadelphus), who, like the American millionaires of to-day, founded a museum where savants were generously supported on the sole condition of furthering science. He also established two great libraries of which Aristotle's works formed the nucleus, and which 50 years after their foundation, contained more than 600,000 manuscripts. In addition to this there was an active trade in manuscripts, favoured by the fact that Egypt possessed the monopoly of papyrus. Thanks to these exceptional conditions, Alexandria quickly became the refuge of students and professors, and even kept in touch with foreign savants. Thus the sciences in all departments made rapid progress, and reached their zenith in the third century B. C.," p. 65.

"The Romans, owing to their essentially practical and political turn of mind, had little appreciation of pure science. They even despised it, and Cicero praises them because, thanks to the Gods, they were not like the Greeks, and knew how to limit the study of mathematics to utilitarian purposes. The mathematical rudiments of which the Roman surveyors had need were borrowed from Greek writings in such a way as to enable them to be used in practice without the aid of theoretical knowledge. When need a rose, specialists were called from Alexandria and shown the measurements to be made. It must have been in this way that Agrippa carried out the cadastral survey of the empire. The fragments which appear in the mathematical compendiums are very poor," p. 92.

"In glancing at the history of humanity, one fact immediately attracts attention. It is the supremacy over all the continents which Europe has been able to win and to keep until the present day. The cause of this supremacy has not been either numerical superiority or a more advanced social organization or even any particular religious and literary ideas. The Chinese, as is well known, were civilized long before the Europeans, and, long before them, were acquainted with the use of the compass and even of gunpowder. The Hindoos, on the other hand, have possessed from the remote past a religion and a literature whose attraction, even to Western minds, is far from being exhausted; and in Central America there existed a state of advanced civilization, which was annihilated by the Spanish conquest. As to numerical superiority, it is sufficient to recall the fact, that even at the present time, either India or China has a larger population than Europe. If the white race has triumphed over other races, it is because it possessed weapons infinitely more formidable than those of its adversaries, and that for commercial transactions it had at its disposal manufactured products far superior to those of other nations. Now, the manufacture of these weapons and products has only been rendered possible through the progressive development of the mathematical and physical sciences of which the Greek nation laid down the principles and established the solid foundations. So it may be be said that if ancient Greece had not created and transmitted rational science to Europe, the latter would never have gained and kept its world supremacy. Doubtless, long before the Greeks, men possessed scientific knowledge, instinctive and practical. Already, in the Stone Age, they knew how to use the lever to move heavy objects, and how to make spears and arrows. At a later Period the Chaldean and Egyptian civilizations witness to a very remarkable technical knowledge; but as we have seen, they did not succeed in creating rational science, that is, in giving a reasoned explanation of natural phenomena and technical processes," p. 105.

"The Greeks, after some hesitation, would only admit as legitimate constructions those which could be made by means of the straight line and the circle, or, in concrete terms, by means of the rule and compass. The objects of plane geometry are thus clearly defined. In dealing with spatial geometry, however, a difficulty at once arises. Solid bodies cannot be represented by a plane drawing without using descriptive geometry. The Greek geometers did not think of having recourse to this expedient, and did not at first know how to get over this difficulty, for which Plato reproaches them very severely. They ended by admitting *a priori* the legitimacy of constructions, which correspond spatially to plane constructions made with rule and compass; the construction of a plane, a straight line or a circle in space, and also of round bodies such as the cylinder, cone, sphere, generated respectively by the revolution of a rectangle, triangle, and circle round a rectilinear axis. At the same time conic sections took their rightful place in geometry, since they could be obtained, as we have seen, by the intersection of a cone and a plane suitably placed. Such curves as the quadratrix of Hippias, the conchoid of Nicomedes and the cissoid of Diocles remained rather on the margin of the pure and officially recognized science; they were considered too mechanical because instruments other than the rule and compass were needed for their construction," p. 116.

"In conclusion, what characterized the spirit and methods of Greek geometry was an ideal of logical rationality which may be defined in the following terms:

1. To postulate primary propositions (definitions, hypotheses) as logical and as few in number as possible.

2. To construct by means of reasoned deduction the whole edifice of mathematics on the basis of these propositions.

"Logical rigour is thus safeguarded, but at the price of complications which, as we have just seen, do not allow the methods of invention and demonstration to be given all the generality of which they are capable," p. 160.

"We know how Copernicus during the Renaissance brought into fame the heliocentric system proposed by Aristarchus, while at the same time, like the latter, he kept the conception of a finite universe. Under these conditions his hypothesis could not have a revolutionary character. Being regarded as a mathematical speculation, it was studied from this point of view and was found wanting, even by thinkers such as Tycho Brahe. It contra-

dicted the physics of Aristotle without supplying the proofs required; moreover it scarcely simplified the calculations at all, since the movement of the planet Venus, for instance, still required a machinery of five epicycles.

"In order to disturb beneficially the minds of men and to find credence, the hypothesis of Copernicus needed to be completed:

1. By the considerations of Giordano Bruno on the relative movements and the infinite magnitude of the universe;

2. By the hypothesis of Kepler regarding the elliptic movement of the planets, a brilliant hypothesis, since it led to a very great simplification in the calculations, without being contrary to the appearances;

2. By the researches of Gaileo on weight, and by his observations on sun-spots; for the results thus obtained finally demolished the physical theories of Aristotle concerning loci and the opposition between the celestial and sublunar regions.

"It was therefore owing to the works of Kepler and Galileo that the mathematical and physical hypotheses could harmoniously blend and that astronomy could enter upon new paths," p. 176.

"In the sciences which we have hitherto considered, observation and practice have, up to a certain point, guided theory. It was not the same with chemistry, the theories of which were closely connected with metaphysics and had no great influence on the technical processes. The first gropings of chemical technique are very ancient. They seem to go back to a prehistoric epoch, to the time when metals were first used for manufacturing weapons, and when certain alloys were perceived to be advantageous. Amongst these alloys, that of tin and copper was specially important. From the most remore antiquity Egypt was an important centre of the trade in tin; which in later times was supplied by Phoenician traders. Other metals were afterwards discovered and alloyed. In Egypt, the method of treating them was preserved by tradition in the form of short and probably mysterious receipts whose secret was jealously guarded by the priests. Certain hieroglyphic signs, completed by oral instructions, were sufficient to ensure the transmission of the methods of manufacture," p. 203.

"As, in the eyes of modern chemistry, an element has an affinity for certain known elements, so the alchemists held the opinion that, although every body can be transmuted into something else, this can only be done by following an invariable order. For example, if F represents iron and O gold, in order to transmute F into O it is necessary to give to F the property G, then by means of G the property H, and so on up to O. If one of the links be omitted, the transmutation will not take place. Hence the famous symbol of the serpent biting its tail," p. 209.

"Compared with the empirical and fragmentary knowledge which the peoples of the East had laboriously gathered during long centuries, Greek science constitutes a veritable miracle. Here the human mind for the first time conceived of the possibility of establishing a limited number of principles, and of deducing from these a number of truths which are their rigorous consequence.

"Beyond the fugitive data of sensation, the Greeks sought for the relationships, which impress the mind as being founded on fact and reason. They were the first to make known the connection of thought and language, and to notice the difference between reasoning and the facts on which it is based.

"This work, begun by Parmenides and the sophists, was carried on by Socrates and Plato, and completed by Aristotle. Parmenides caught a glimpse of a realm of truth unshaken by changing opinions; the sophists laid the foundations of grammar; Socrates established the relationship which exists between the general idea and particular ideas contained in it. Plato distinguished two dialectic processes in the realm of thought, the one which proceeds from hypotheses to consequences, the othere which starting from hypotheses goes back to the principles which justify them. Finally, Aristotle, in the imposing edifice of his logic, co-ordinates the results obtained by his predecessors. In no other civilization and amongst no other nation do we find any similar systematic and rational analysis of human thought," p. 217.

"We are forced to the following conclusion: the physics of relativity in returning to the immediate data of sensible experience seeks to reduce them to axioms, and for this reason it comes into line with the realistic and logical tendencies of the Greek thinkers of antiquity," p. 228.

Wilder D. Bancroft

Makers of Science. *Electricity and Magnetism. By D. M. Turner. 20 × 13 cm; pp. xv + 184. London: Oxford University Press, 1927. Price: $2.50.* In the introduction by Charles Singer, we read, p. xiii: "There is a common idea, a wholly base idea it seems to me, that Science in these latter days has so advanced that no man can survey it as a whole. If it were so—and I for one disbelieve it—that would be good cause to exclude Science from our educational system; for what does not clarify—which, being interpreted, is but to unify—what does not help a man to ascend the heights of reason that he may behold the world at his feet, cannot aid him in understanding the world in which he lives. If it were so that no man can survey all Science, then the sole plea for Science in education would be its practical application, and Science would be numbered among the crafts and tricks of life. It would be of purely vocational value. It is an unworthy and I believe an untrue view of Science, which would rob it of all spiritual value.

"If this view were pressed, it would not only prevent the writing of the History of Science, but would also prevent the writing of both History and Science. Who, of his own knowledge, can compass the history of even a single country? Who, of his own knowledge, can deal with the Animal Kingdom, with the Science of Geometry, or with our knowledge of the Structure of the Earth? Yet these limitations have not prevented, and should not prevent, the writing of Histories of England and of Europe, of works of Zoology, of treatises on Mathematics, or of text-books on Geology. The scope of such books in reference to the direct experience of the individual writer must be effectively infinite. The difficulty of writing them is the difficulty of getting a philosophical grasp of the principles involved, and in obtaining such grasp first-hand knowledge is of primary importance. Yet this knowledge applied in such a field is but a means to an end, and the work must be judged by the grasp of the principles that it sets forth rather than by the mere knowledge of detail that it displays.

"The truth is that there never was a time when one man could know *all* that was known about his world. In this respect our age is even as other ages were, and it is a sheer illusion to suppose that it differs from them in this regard. Nor is the advance of Science to be measured by the vast accumulation of observations, but by the degree to which these observations are brought under general laws. The function of Science is to clarify, which is to simplify and ultimately to unify. It is just by its success in unifying our conception of the Universe that the state of Science must be gauged, and not by the number of professors that it employs. I believe that, in fact, a general view *can* be acquired of the state of our scientific knowledge, and that the provision of that view should be an important function of our educational system," p. XIII.

The chapters are entitled: early speculations; electro-statics in the eighteenth century; the electric current; electro-magnetism; the discovery of electro-magnetic induction; electrical measurements and some practical application; development of electrical theory; electrolysis; and conduction of electricity through gases; electrical constitution of matter.

The reviewer marked eight passages which interested him especially. They will not be cited because they might not interest anybody else. Others will find other passages which will appeal to them. Two quotations will give some idea of the general style of the book.

"The researches of Faraday afford an excellent example of true scientific method. Faraday began by making himself absolutely familiar with the whole field of knowledge of electrical and magnetic phenomena then existing. He never proceeded in a haphazard fashion, but always with some definite object in view. He succeeded where other men failed because, apart from his untiring energy and desire for truth, he had the insight of genius and saw possibilities where lesser men would have groped in confusion. Faraday did not

stop when he had succeeded in making a magnet rotate round a current and a current round a magnet; he felt that there must be some relation between these rotations and those noticed by Arago. He felt that the action of a current on a magnet noticed by (Oersted, and that of current on current noticed by Ampère, must be due to some common cause. The discovery of this cause might give the clue to the reason for electro-magnetic rotations and other phenomena. It must be remembered that although Ampère had come forward with a mathematical theory of electro-magnetism, the ideas held by scientific men at the time were very hazy. Oersted, as we have seen, had spoken of the 'conflict of electricty'. Others had dealt with the forces acting circumferentially round a wire carrying current. But in every case the force was looked for in the actual conductor or in the magnet, as the case might be.

"Faraday introduced a new conception with the subject. He conceived the forces to be due to tensions and strains in the *medium* surrounding the magnet or conductor. He was no mathematician, and problems were not solved for him when they were expressed in mathematical language, so that he seems to have needed some means of visualising the actual physical conditions taking place. It was for this reason that he put forward his conception of lines of force, but before we can appreciate the importance of this conception, we must go back and consider his experiments in detail," p. 90.

"The Electro-magnetic Theory of Light was a shock to the sensibilities of some of the more conservative physicists, who were reluctant to abandon the obliging elastic solid ether which had served them so long and so faithfully. Lord Kelvin in particular was unwilling to accept the newer views. But Maxwell's investigations brought about a great simplification in electrical theory. His "Treatise on Electricty and Magnetism," published in 1873, is a landmark in the history of science. The wide and philosophical outlook evident throughout the whole work, despite the difficulties of the mathematical exposition, has remained a source of inspiration to all workers in physical science," p. 136.

Wilder D. Bancroft

Old Chemistries. *By Edgar F. Smith. 25 × 19 cm; pp. x + 89. New York: McGraw-Hill Book Company*, 1917. "What excuse shall be offered for writing this book? Its object is to lay before interested readers a hint of the vast stores of early literature relating to chemistry, of which many are ignorant. It may be that the few volumes alluded to in the following pages will elicit further search along similar lines.

"The author's hope is that sometime—how soon he knows not—but, sometime—the history of chemistry will be given its place in the curriculum of studies in every institution of learning where the science itself is studied; for it is, indeed, a very comprehensive subject," p. VII.

No justification is necessary for any book by Edgar F. Smith and this volume is no exception. The following are a few of the items that appealed especially to the reviewer. Jean Beguin's *Tyrocinium Chymicum* (1643) passed through no fewer than fifty-three editions, p. 3. George Wilson published "A Compleat Course of Chemistry" in 1709. "I have thro' the whole studied *Brevity*, and therefore I have rejected not only the frivolous and useless Trifles of other Chymical Authors, and also have declined Mons. Lemery's pompous way of Philosophyzing upon the Processes. Neither was it my business to criticize upon that celebrated Author; but let the judicious Reader compare our Methods of working the same Subject, and he will in some things find a wide Difference, which I am content shall be put to the test of Practice, and then you will soon determine who is in the right," p. 7.

Rush's "Syllabus" (1770) was the first textual contribution in chemistry from the hand of an American. Richard Watson was elected professor of chemistry at Cambridge University in 1762 and professor of divinity in 1771. In 1781 he published his "Chemical Essays," in which he says, p. 17, "I hope the utility of the design will plead my excuse with those who, in the severity of their judgments, may think that I have contributed more than, from the nature of my Profession and situation, I ought to have done. When I was elected Professor of Divinity in 1771, I determined to abandon forever the Study of Chemistry, and I did abandon it for several years; but the *veteris vestigia flammae* still continued to de-

light me, and at length seduced me from my purpose. When I was made a Bishop in 1782, I again determined to quit my favorite pursuit; the volume which I now offer to the public is sad proof of the imbecility of my resolution. I have on this day, however, offered a sacrifice to other people's notions, I confess, rather than to my own opinion of Episcopal Decorum—I have destroyed all my chemical Manuscripts."

In 1790 Penington published his "Chemical and Economical Essays." "Chemists themselves belong to two great and distinct classes, which, it is a pity are not connected; in the one class we may rank those who perform a great number of operations by heat and mixture, without ever knowing the secondary causes of the effects produced; these are called practical chemists, such as dyers who cannot account for, or conceive why, allum, for instance, should be of use in their art; or why galls and copperas should produce a black dye; such also are tanners, who cannot explain the action of the oak bark on the hides; such likewise are many apothecaries, who can make aqua fortis, etc., etc., but know nothing of the rationale of the process; the other class is represented by the mere theorist, who is well acquainted with the "effects of heat and mixture" upon all bodies, and can account for them all, but never soils his fingers with a piece of charcoal, or has had occasion to break a crucible; such a chemist can inform us admirably how the changes of colour in dying are produced, but would be unable to produce them himself; he can account for the action of oak bark upon animal substances, without ever having smelt the odour of a tan-yard; he could explain the theory and process of making aqua fortis; and perhaps were he to attempt to make it, he would be two hours kindling a fire in his furnace, break his distillery apparatus, lose all his aqua fortis, and suffocate himself with the fumes. From the comparison every one will allow that the practical chemist is the most respectable character; but many worthy gentlemen of this class have contended, that theoretical chemistry could be of no use to them. This idea, however, will admit of much dispute; if we appeal to fact, we find that many of the most useful discoveries in the arts have been made by men who have combined some kind of theory with their practice," p. 20.

Lavoisier's "Elements of Chemistry" was published in 1789. In a letter to Franklin he says, p. 32, that "the French scholars are divided at this moment between the old and the new doctrine [phlogiston and oxygen.] I have on my side M. de Morveau, M. Berthollet, M. de Fourcroy, M. de la Place, M. Monge, and in general the physicians of the Academy. The scholars of London and of England have unconsciously abandoned the doctrine of Stahl, but the German chemists adhere to it."

Wilder D. Bancroft

The Chemistry of Dyeing. *By John K. Wood. New and revised edition. 18 × 13 cm; pp. vii + 104. London: Gurney and Jackson, 1926. Price: 3 shillings, 6 pence.* The chapters are entitled: the chemical composition and properties of the textile fibres; dyes and their properties; the nature of the dyeing process. The last chapter is the long one, 67 pages. In the preface to this edition the author says that this chapter, in particular, contains "a considerable amount of new matter and has been modified in other ways so as to present as up-to-date an account as possible of the views held with respect to the process of dyeing."

The author has read the modern work on the theory of dyeing; but it apparently has not registered, because he discusses and contrasts the chemical theory, the solution theory, the mechanical theory, the adsorption theory, the colloid theory, and the electrical theory. If one takes the so-called mechanical theory, as the author does, in the tentative form suggested by Hellot, it is legitimate to consider it as a separate theory. If one considers Crum an upholder of the mechanical theory, as most people do, the mechanical theory is merely an early form of the adsorption theory because Crum is quite explicit as to the process being similar to the holding of gases by charcoal. To put forward a colloid theory or an electrical theory as differing from an adsorption theory would be a joke if it were not so pathetic. There are only three ways in which a dye can be held by the fiber, so far as we now know. We may have a definite chemical compound, a solid solution or an adsorption. Everything else is a matter of detail and not fundamental.

Wilder D. Bancroft

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22-63

THE ADSORPTION OF GASES BY SOLIDS WITH SPECIAL REFERENCE TO THE ADSORPTION OF CARBON DIOXIDE BY CHARCOAL

BY H. H. LOWRY AND P. S. OLMSTEAD

Introduction

Although many attempts[1] have been made to develop a theory of adsorption of gases by solids which will allow quantitative prediction of the effect of changes in temperature and pressure on the quantity of gas adsorbed by a given adsorbent, none of the theories, with the possible exception of that of Polanyi, may be said to be satisfactory. This is due to the fact that the mathematical relationships resulting from the various theories have all contained constants which cannot be directly determined; as a result there now exist many empirical equations which fit almost equally well the data obtained either at constant temperature, or at constant pressure, or with constant amount adsorbed. Polanyi's theory, on the other hand, assumes that the force of attraction of the solid adsorbent for the gas molecules decreases with increasing adsorption in a way which is characteristic of the adsorbent, but which is independent of temperature and can be determined from a single isotherm. The amount of gas adsorbed at any other temperature or pressure can then be calculated if the way in which the volume and intermolecular attraction of the gas change with temperature and pressure is known. Although these relationships are given in an equation of state, it is very difficult to apply to experimental data the theory of adsorption as developed originally by Polanyi and later by Berenyi.

[1] The following references include only papers since 1910 in which a theory of adsorption is developed and presented mathematically in a form which allows application to experimental data:

a. I. F. Homfray: Z. physik. Chem., **74**, 129 (1910).
b. G. C. Schmidt, Z. physik. Chem., **74**, 704 (1910); **77**, 646 (1911); **78**, 667 (1912); **83**, 674 (1914).
c. S. Arrhenius: Meddel. fr. K. Vet. Akad. Nobelinst (2), M. 7, (1911).
d. A. M. Williams: Trans. Faraday Soc., **10**, 167 (1914); Proc. Roy. Soc. Edin., **38**, 23 (1918); Proc. Roy. Soc., **96A**, 287 (1919).
e. A. Eucken: Verh. deutsch. physik. Ges. **16**, 345 (1914); Z. Elektrochemie, **28**, 7, 257 (1922).
f. M. Polanyi: Verh. deutsch. physik. Ges., **16**, 1012 (1914); **18**, 55 (1916); Z. Elektrochemie, **26**, 370 (1920); **28**, 110 (1922).
g. I. Langmuir: Phys. Rev., (2), **6**, 79 (1915); **8**, 149 (1916); J. Am. Chem. Soc., **40**, 1361 (1918); see also D. Reichinstein: Z. physik. Chem., **107**, 119 (1923).
h. L. Berenyi: Z. physik. Chem., **94**, 628 (1920); **105**, 55 (1923); Z. angew. Chem., **35**, 237 (1922).
i. D. C. Henry: Phil. Mag., **44**, 689 (1922).
j. R. Lorenz and A. Lande: Z. anorg. Chem., **125**, 47 (1922).
k. B. Iliin: Z. physik. Chem., **107**, 145 (1923); **116**, 431 (1925); J. Russ. Phys. Chem. Soc. **56**, 2 (1924); Phil. Mag., **48**, 193, (1924); **50**, 1144 (1925); Z. Physik, **33**, 435 (1925); Physik. Z., **26**, 497 (1925); **27**, 591 (1926); see also H. Cassel: Physik. Z., **26**, 862 (1925).
l. W. Tarassoff: Physik. Z., **25**, 369 (1924).
m. A. Gorbachev: Z. physik. Chem., **117**, 129 (1925).
n. E. Jaquet: Fortschritte Chem., **18**, 437 (1925).
o. A. Magnus: Z. anorg. Chem., **158**, 67 (1926).

This difficulty has led us not only to present briefly in this paper a physical interpretation of the theory of adsorption and its mathematical development, both of which differ somewhat from those given by Polanyi, but also to show in considerable detail a relatively convenient method of application to the experimental data. Using the procedure outlined in this paper, a test of the theory has been made on the data obtained by Homfray, Titoff, Richardson, Chappuis and S. O. Morgan for the adsorption of carbon dioxide by charcoal. The very satisfactory agreement between experiment and theory gives support to the fundamental assumptions underlying the theory.

For convenience in reference we give the following lists of the symbols and their definitions, and of the constants and their numerical values which are used in the following discussions:

Definition of Symbols

$\varphi_{Max.}$	cu. mm.	"Limiting adsorption volume," that is, the volume occupied by adsorbed gas which is equal to the effective surface of the adsorbent multiplied by the distance from the surface at which the forces of adsorption are unable to bring about any increase in concentration of the surrounding gas.
φ_s		"Calculated adsorption volume at a particular temperature and pressure," that is, the volume occupied at any particular temperature and pressure by that part of the adsorbed gas in which the molecules are as close as or closer than they are in the liquid state at that temperature. φ_s approaches $\varphi_{max.}$ as the temperature approaches 0°K.
$d\varphi$		Differential of volume in the adsorbed gas.
s		Subscript denoting the level separating densities less than that of the liquid at a particular temperature from those higher than that of the liquid.
δ	gr. per cc	Density in any $d\varphi$.
δ_x		Minimum density in the surrounding gas atmosphere.
δ'		Average density of the adsorbed gas within φ_s for the temperature and pressure at which x was measured.
x	mg per gr. of carbon	Mass of adsorbed gas.
$x_{obs.}$		Observed value of x at a particular temperature and pressure.
$x_{cal.}$		Calculated value of x for a particular temperature and pressure.
$x_{corr.}$		That part of $x_{obs.}$ which corresponds to x_s.
Δx		Mass of adsorbed gas compressed into a small volume $\Delta\varphi$ of density δ.

ϵ	calories per gram molecule of adsorbed gas	"Adsorption potential," that is, the energy required to compress a gram molecule of the gas atmosphere to the density δ at which some Δx exists on the surface of the adsorbent.
$\Delta\epsilon$		Energy necessary to compress a gram molecule from V_{δ_x} to $V = 1$.
i		Subscript denoting a variable level.
V	gram molecular volume	Volume.
P	atmospheres	Pressure.
T	°K	Temperature.
T_c	°K	Critical temperature.
R	calories per degree K	Gas Constant.
a, b		Constants from van der Waals' equation.
α		Constant appearing in relationship of a to T.
$(b_g)_T$		Value of b for $V = \infty$ at temperature T.
$(b_o)_T$		Value of b for $P = \infty$ at temperature T.
e		Base of natural logarithms.

Table of Constants[2]

R = 1.9876 cal. per degree Kelvin = 0.0036618 GMV atmos/deg.
$\log_e = 2.3026 \log_{10}$
0°C = 273.09°K
GMV = 22416 cc.
$J = 4.184 \cdot 10^7$ ergs. per cal.
1 atmo. = $1.01320 \cdot 10^6$ dyne/cm²

Physical Interpretation of the Theory

The fundamental assumption underlying the theory of adsorption is that there is a force of attraction between dissimilar molecules. That such a force exists between similar molecules is the conclusion reached in considering such phenomena as: the heat of vaporization; van der Waals' constant a; surface tension; etc. It seems, therefore, quite reasonable to assume that a similar force exists between molecules of different types even if they are in different states of aggregation. That it is exhibited by different molecules in the same state of aggregation follows directly from van der Waals' theory of mixtures.

If it is assumed that the force between the molecules takes the form of an intermolecular potential gradient, it is possible to develop a theory of adsorption similar to that of Eucken[1e]. This has been found sufficient for the explanation of adsorption at small gas pressures and for gases at temperatures above their critical temperatures. At these pressures and temperatures real and ideal gases are much alike and the results to be expected for an ideal gas

[2] The values of these constants are those given by van Laar in "Zustandsgleichung," (1924).

are obtained. In general, however, theory and experiment do not check at high gas pressures nor at temperatures below the critical, indicating that in order to include real gases at all temperatures and pressures in a complete theory of adsorption the equation of state must be considered.

To do this it is possible to follow the outline given by Polanyi[1f] and Berenyi[1h]. They have considered a solid adsorbent existing in an atmosphere of gas. For this system the fundamental assumption may be interpreted to mean that there is a force of attraction between the adsorbent and the atmosphere of gas which surrounds it. This force, which may be assumed to be dependent on the kind and separation of the mutually acting molecules and independent of the temperature over the temperature ranges usually considered in adsorption (i.e., 80 to 500°K), is exhibited in the gas atmosphere by changes in density. If the temperature is sufficiently below the critical temperature of the gas, the concentration of molecules may be as great as, or greater than, it is in the liquid, or the solid, state at that temperature. Because of this, the "limiting adsorption volume," $\varphi_{max.}$ may be defined as the maximum volume which may be occupied by adsorbed gas in which the gas molecules are as close as or closer than they would be in a liquid at that temperature. It is convenient to determine this volume from experimental data obtained at some temperature well below the critical temperature and at some pressure of surrounding gas below, but very near the saturation pressure, since near the saturation pressure and well below the critical temperature a very small amount of energy is necessary to cause liquefaction. Since neither the surface of the adsorbent nor the distance through which the forces of adsorption act can be accurately measured, the limiting adsorption volume must be determined by some means such as indicated.

For any particular temperature and pressure, that part of φ_{max} within which the molecules are as close as, or closer than, in a liquid at that temperature will be called the "calculated adsorption volume," and will be designated by φ_s. At very low temperatures one may well assume that the adsorbed gas is almost entirely within the volume φ_s since within this volume the density will greatly exceed the density in the surrounding atmosphere. However, since φ_s decreases very markedly with increase in temperature and since most measurements of adsorption have been made at relatively high temperatures, it is necessary to consider not only φ_s, but the whole region $\varphi_{max.}$[3]

The statements made in the preceding paragraph may be best understood by considering the distribution of density within the limiting adsorption volume. This may be shown by three typical cases, as in Fig. 1, in which δ is plotted as a function of φ. Curve 1 is an example of a gas adsorbed at a pressure near saturation and at a temperature well below its critical temperature. It indicates the densities through the adsorbed volume when the at-

[3] For temperatures above the critical temperature, φ_s must be given a slighly different interpretation, because the molecules can no longer exist in the liquid state. In such cases it is sufficient to consider that part of φ_{max}, within which the molecules are as dense or denser than the density corresponding to the extrapolated saturation pressure at those temperatures.

tractive forces are sufficient to keep all adsorbed molecules as close together as they are in a liquid, i.e. when all the adsorbed gas lies within φ_s. Curve 3 shows the distribution in densities when it is never possible to have the molecules as close together as they are in a liquid. This represents the distribution at temperatures well above the critical temperature. The more general type of curve, such as is ordinarily obtained with carbon dioxide, is characteristic of the intermediate range of temperatures and is represented by Curve 2, in which, although φ_s is less than one-half $\varphi_{max.}$ by far the greater part of the adsorbed gas lies within φ_s. It is obvious that the quantity of gas adsorbed may be obtained by integrating $(\delta - \delta_x)d\varphi$ between the limits o and φ_{max}, or

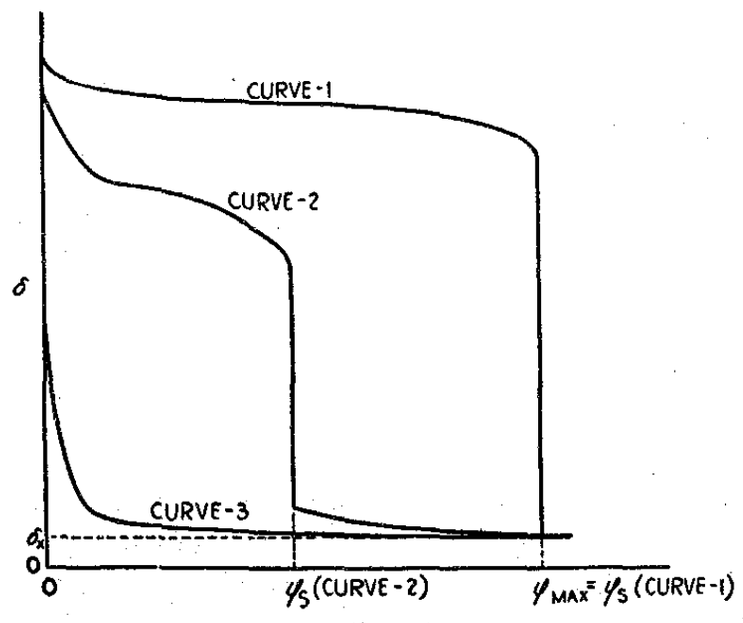


FIG. 1
Typical δ-φ Curves

$$x = \int_0^{\varphi_s} (\delta - \delta_x)\, d\varphi + \int_{\varphi_s}^{\varphi_{max}} (\delta - \delta_x)\, d\varphi = \int_0^{\varphi_{max}} \delta d\varphi - \delta_x \varphi_{max}. \qquad (1)$$

or, since under most experimental conditions, δ_x is small and may be neglected,

$$x = \int_0^{\varphi_{max}} \delta d\varphi \qquad (2)$$

At high temperatures or high pressures it is sometimes necessary to retain $\delta_{max.}$

In order to determine the energy which must be expended in compressing the gas taken from the surrounding atmosphere to the density distribution it has in the adsorption volume, use must be made of the equation of state. This equation is an expression of the way in which the density may be expected to vary with temperature and pressure. Mathematically the total energy necessary for the compression is given by the following expression:

$$\text{Energy} = \sum_{0}^{x} K\left[\int_{\delta_x}^{\delta} V\,dP\right]\Delta x = \sum_{0}^{x} K\epsilon\Delta x, \tag{3}$$

$$\text{where, } \epsilon = \int_{\delta_x}^{\delta} V\,dP, \tag{3a}$$

and K is a proportionality factor correcting Δx to gram molecules. In this expression ϵ, which has been called the "asdorption potential," represents the energy required to compress a gram molecule of the gas atmosphere to the density δ at which some small mass Δx exists on the surface of the adsorbent. This energy is a result of the attractive force of the adsorbent for the surrounding gas. Some equation of state must be assumed before the value of this integral can be obtained.

Physically the process of adsorption, as outlined by this theory, may be pictured as consisting of the filling of a number of small volumes $\Delta\varphi_i$ with gas at a pressure large enough to compress the gas to a density δ_i. Since a potential

$$\epsilon_i = \int_{\delta_x}^{\delta_i} V\,dP, \tag{4}$$

exists at the ith cell and the potential where the density is δ_x is o, it follows that after $(i - 1)$ cells are filled a difference of potential $\epsilon_i - o$ remains to draw molecules into the ith cell. Equation (4) is an expression for the potential which by assumption depends only on the kind and separation of the mutually acting molecules. This makes the quantity a function of volume only, or $\epsilon = f(\varphi)$. The additional assumption has been made that for gases which are not associated (that is, do not form double molecules), this distribution of potential is independent of temperature.

Development of the Theory

As a result of the discussion in the last section, the relationship between the adsorption potential, ϵ, and volume, φ, of gas adsorbed is seen to be an important one. By the use of an equation of state this $\epsilon - \varphi$ relation may be determined for a given adsorbent and gas from the observed values of the amount of adsorbed gas, the pressure of the external gas atmosphere and the temperature of the system. Since the relationship between ϵ and φ is assumed to be independent of temperature, it is theoretically possible to obtain a complete curve at any temperature. However, if measurements are limited to pressures below one atmosphere, the complete curve is not obtained at high temperatures because the amount of gas adsorbed is relatively small, i.e., φ is small; at low temperatures, the $\epsilon - \varphi$ curve can generally be determined only for large values of φ, because a large amount of gas is adsorbed before the pressures can be read accurately (i.e., pressures less than 1 mm). In equation (4) the relationship between the quantity ϵ and others which may be

measured is shown. Each value of φ must be obtained at a point corresponding to a particular value of ϵ. This is given by the upper limit of the integral in the expression

$$x_i = \int_0^{\varphi_i} \delta d\varphi \qquad (5)$$

which, of course, is similar to equation (2a). Of the factors in equations (4) and (5), P, V, δ,[4] and δ_i are related by an equation of state. In general, x_i cannot be calculated until some knowledge of the relationship between δ_i and φ_i is obtained. For a particular temperature T and external gas pressure P, δ_i may be secured as a function of ϵ_i from equation (4). On the other hand, φ_i must be determined from observed values of x and from some estimate of the way in which δ varies with φ.

This leads to approximations from which a provisional $\epsilon - \varphi$ curve may be obtained. At temperatures well below the critical temperature, most of the adsorbed gas has a density equal to or greater than that of the liquid. For a first approximation, the minimum density of the liquid at the temperature of the experiment may be substituted for the average density of the adsorbed gas. Using this and the observed values of x, values of φ may be obtained by the equation,

$$x_{obs.} = \varphi_s \delta' \qquad (6)$$

where δ' is the average density of the adsorbed gas within the volume φ_s for the temperature and pressure at which x was measured. Values of ϵ at corresponding densities (δ_x) may be computed from equation (4).

From a temporary $\epsilon - \varphi$ curve obtained in this way and a $\delta - \epsilon$ curve obtained from equation (4) and the PV data, it is possible to use simultaneous values of δ and φ to calculate x and x_s. If $x_{cal.}$ is identical with $x_{obs.}$ for all values, the temporary $\epsilon - \varphi$ curve may be considered final. If disagreements occur, certain corrections may be made. The average density corrected for the calculated x_s is given by the equation

$$x_s = \varphi_s \delta'. \qquad (7)$$

A corrected value of x_s may be obtained by the relationship:

$$x_{corr.} = x_s \cdot \frac{x_{obs.}}{x_{cal.}}. \qquad (8)$$

The value of $x_{corr.}$ may then be used in equation (6) with the corrected value of δ' to determine φ_s. The $\epsilon - \varphi$ curve determined by this calculation is a second approximation. Generally not more than two corrections are necessary to obtain the final curve.

In order to find the values of ϵ_i by equation (4), a knowledge of the relationship between P and V is necessary. Values of PV as a function of P and T are given for a large number of gases in Landolt-Börnstein.[5] For the

[4] See note 9.

[5] Landolt-Börnstein: "Physical and Chemical Tables," (1923).

purpose of this work, these cover a relatively small range of T and P. It is, therefore, necessary to determine, by extrapolation or otherwise, values of PV for other temperatures and pressures. Van der Waals' equation,[6] which is often used for this extrapolation, is not of sufficient accuracy in all cases.

For certain gases, van Laar[7] has shown that, for a wide range of pressures and temperatures, the following relationship holds:

$$\left[P + \frac{a_T}{V^2}\right]\left[V - \frac{(b_g)_T}{1 + \frac{(b_g)_T - (b_o)_T}{V}}\right] = RT, \qquad (9)$$

$$\text{where } a_T = a_{Tc} e^{\alpha\left(\frac{1}{RT} - \frac{1}{RT_c}\right)} \qquad (10)$$

a_{Tc} is the value of van der Waals' a determined from the critical data, α is a constant, and

$$\frac{(b_g)_T}{1 + \frac{(b_g)_T - (b_o)_T}{V}} = \text{van der Waals' b at temperature T}, \qquad (11)$$

where $(b_g)_T$ is the value of b at $V = \infty$
and $(b_o)_T = b = V$ at infinite compression.

From equation (4) one may obtain,

$$\epsilon_i = \int_{\delta_x}^{\delta_i} V dP = \Big[PV\Big]_{\delta_x}^{\delta_i} - \int_{\delta_x}^{\delta_i} P dV \qquad (12)$$

Substituting the value of P from equation (9), this becomes

$$\epsilon = \left[\frac{RT\,[V + (b_g)_T - (b_o)_T]}{[V - (b_o)_T]} - \frac{a_T}{V}\right]_{\delta_x}^{\delta_i} - \int_{\delta_x}^{\delta_i}\left[\frac{RT\,[V + (b_g)_T - (b_o)_T]}{V\,[V - (b_o)_T]} - \frac{a_T}{V^2}\right] dV. \qquad (13)$$

Then since

$$\int_{\delta_x}^{\delta_i}\left[\frac{RT\,[V + (b_g)_T - (b_o)_T]}{V\,[V - (b_o)_T]} - \frac{a_T}{V^2}\right] dV =$$

$$\int_{\delta_x}^{\delta_i}\left[\frac{RT\,[(b_o)_T - (b_g)_T]}{(b_o)_T\ V} + \frac{RT\,(b_g)_T}{(b_o)_T\,(V - (b_o)_T)} - \frac{a_T}{V^2}\right] dV =$$

[6] The use of van der Waals' equation at constant temperature where the constants a and b can be directly determined from PV data as recommended by Berenyi (Ref. 1h) for a test of the Polanyi theory of adsorption, is not satisfactory since the values of a and b are dependent on the pressures used in determining the values of PV. The particular values of these constants used by Berenyi are not given in his paper. This makes it almost impossible to check his calculations for comparison with other data.

[7] Van Laar: "Zustandsgleichung von Gasen und Flüssigkeiten," (1924).

$$\left[\frac{[(b_o)_T - (b_g)_T]\ RT\log_e V}{(b_o)_T}\right]_{\delta_x}^{\delta_i} + \left[\frac{RT(b_g)_T}{(b_o)_T}\log_e [V - (b_o)_T]\right]_{\delta_x}^{\delta_i} + \left[\frac{a_T}{V}\right]_{\delta_x}^{\delta_i} \quad (14)$$

a complete solution of equation (12) is:

$$\epsilon_i = RT\left[\frac{(b_g)_T}{V - (b_o)_T} - \frac{2a_T}{RTV} - \log_e V - \frac{(b_g)_T}{(b_o)_T}\log_e\left[1 - \frac{(b_o)_T}{V}\right]\right]_{\delta_x}^{\delta_i} \quad (15)$$

When equation (15) is applied to observed data a number of simplifications may be made. Almost all measurements are made at pressures less than one atmosphere and a relatively small error will be introduced by neglecting a_T, $(b_o)_T$ and $(b_g)_T$ with respect to V for $\delta = \delta_x$. Introducing the proper constants the value of ϵ_i is then given by

$$\epsilon_i = 4.5767\ T\left[\frac{0.4343\ (b_g)_T}{V_{\delta_i} - (b_o)_T} - 237.213\frac{a_T}{TV_{\delta_i}} - \log V_{\delta_i} - \frac{(b_g)_T}{(b_o)_T}\log\left[1 - \frac{(b_o)_T}{V_{\delta_i}}\right] + \log V_{\delta_x}\right]. \quad (16)$$

From this equation two others which are of interest in special cases may be obtained. If $a_T = a$ and $(b_g)_T = (b_o)_T = b$, the equation of state reduces to the usual van der Waals' equation and equation (16) becomes

$$\epsilon_i = 4.5767\ T\left[\frac{0.4343\ b}{V_{\delta_i} - b} - 237.213\frac{a}{TV_{\delta_i}} - \log V_{\delta_i} - \log\left[1 - \frac{b}{V_{\delta_i}}\right] + \log V_{\delta_x}\right] \quad (16A)$$

which is similar to those obtained by Berenyi and Polanyi.[8] If the equation of an ideal gas is assumed, a = b = 0 and this equation may be written

$$\epsilon_i = 4.5767\ T\left[\log V_{\delta_x} - \log V_{\delta_i}\right]. \quad (16B)$$

From equation (16) and $\epsilon - \delta$ distribution may be obtained for any δ_x. In practice, the distribution for δ_x which gives V = 1[9] is obtained first. That for any other δ_x is obtained by a change in ϵ which is independent of δ:

$$\Delta\epsilon = 4.5767\ T\log V_{\delta_x} \quad (18)$$

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[8] Berenyi: Z. physik Chem., **94**, 632 (1920); Polanyi: Verh. deutsch. physik. Ges., **18**, 64 (1916).

[9] For carbon dioxide V is related to δ_x by the equation

$$\frac{V}{.994599} = \frac{M}{22416\delta_x} \quad (17)$$

where M is the molecular weight. The numerical factor on the left side is determined from van Laar's modified van der Waals' equation for P = 1, and RT = 1 that is, for T = 273.09°K. It represents a correction to be applied to the gram molecular volume at 0°C. and 760 mm. Hg pressure to make it conform with the volumes used in the equation of state. This factor differs with different gases.

These $\epsilon - \delta$ curves are used with the preliminary $\epsilon - \varphi$ curve in determining the calculated value of x. This leads finally to a $\epsilon - \varphi$ curve which represents points determined from observations at a large number of temperatures and pressures.

The Heat of Adsorption

In equation (3) an expression was given for the total work involved in compressing the adsorbed gas from the density at which it exists in the gas atmosphere to the density distribution on the adsorbed volume. If this is divided by the mass of adsorbed gas, the work done in compressing one gram molecule of the gas is obtained.

$$\frac{\sum_{0}^{x} \epsilon \Delta x}{x} = \text{work done per gram molecule.} \qquad (19)$$

This represents the heat of adsorption. When data become available, its value may be compared with experimental results.

Application of the Theory to Data on the Adsorption of Carbon Dioxide by Charcoal

In order to show how the relationships obtained may be applied to experimental results on adsorption, several typical calculations will be explained. It is necessary to find the relations existing, at particular temperatures, among ϵ, φ, δ, P_x and x. Since the PV data on carbon dioxide are the most complete, and there is a large amount of data on the adsorption of carbon dioxide by charcoal, this case was chosen for special investigation.

Van Laar[10] has shown that the P-V data for carbon dioxide may be represented quite accurately by equation (9).[11] Since this is so, equation (16) may be used in obtaining values of ϵ_i for V = 1 at various levels of δ_i for the

[10] See note (7).

[11] Values of a_T, $(b_g)_T$, and $(b_o)_T$ for CO_2 have been calculated from Amagat's PV data (Ann. Chim. Phys. (6), **29**, 68 (1893)) over the range 0° to 198°C. and 1 to 1000 atmospheres pressure. It was found that the values of a_T can be satisfactorily expressed by the equation

$$a_T = 0.007285\, e^{1.2138\left(\frac{1}{RT} - 0.8980\right)} \qquad (20)$$

The dependence of $(b_g)_T$ on temperature is given by the equation

$$\log (b_g)_T = \frac{184.86}{T} - 3.2232 \qquad (21)$$

While the values obtained for $(b_o)_T$ lay on a smooth curve when plotted against T, except for the points at 313.1° & 471.1°, they could not be readily fitted by a simple interpolation formula. In the following table is given a comparison of $\log (b_g)_T$ obtained from equation (21) and from the PV data directly, together with the values of $(b_o)_T$ obtained from the same data.

T	$\log (b_g)_T$ from (21)	$\log (b_g)_T$ from PV data	$(b_o)_T$ from PV data
273.1	−2.5463	−2.5474	1.1468×10^{-3}
293.1	−2.5925	−2.5926	1.0680
313.1	−2.6328	−2.6298	[1.1878]
333.1	−2.6682	−2.6683	1.2208
353.1	−2.6997	−2.7012	1.2554
410.1	−2.7724	−2.7724	1.3566
471.1	−2.8308	−2.8068	[1.4058]

temperatures used. These are given in Table I together with the values of RT, a, b_g, and b_o used in equation (9) for each temperature. Values of ϵ_i are omitted for densities greater than the maximum density of the gas and less

TABLE I

Calculation of ϵ as a Function of δ

δ_i	V_{δ_i}	196.6° ϵ_i	273.1° ϵ_i	373.1° ϵ_i
.0055		450		
.01	195.2×10^{-3}		857	1193
.05	39.05		1612	2312
.08	24.40		1779	2607
.09			1820	
.1	19.52			2737
.3	6.508			3243
.5	3.905			3417
.591				3505
.7	2.789			3634
.9	2.169			4112
.91			1820	
1.0	1.952		1985	4566
1.1	1.775		2325	5302
1.2	1.627		2912	6582
1.25		450		
1.3	1.502	884	3925	9142
1.4	1.394	2233	5785	
1.5	1.302	5094	9620	
1.6	1.220	11112		
	RT	.7199	1.000	1.366
	a	.01322	.008245	.005955
	b_g	.005214	.002836	.001868
	b_o	.001089	.001147	.001289

than the minimum density of the liquid. Values of ϵ_i greater than ϵ_s are corrected by the value of the difference in ϵ between the value for the gas at maximum density and the value for the liquid at minimum density. This correction should be zero. In practice the minimum value of ϵ_i for maximum density of gas is seldom identical with that for minimum density of the liquid. Thus, at 196.6°C, the value of ϵ_i at $\delta_i = 1.25$ is taken equal to that at $\delta_i = .0055$. This value of ϵ_i is the value of ϵ_s at that temperature for $V = 1$.

To find the value of ϵ_s at temperatures above the critical temperature, use is made of the empirical equation originally proposed by van der Waals',[12] which relates the temperature and pressure at which liquefaction takes place

$$\log \frac{P_c}{P} = 2.89 \left(\frac{T_c}{T} - 1\right) \qquad (22)$$

[12] See van Laar: loc. cit., 218 ff.

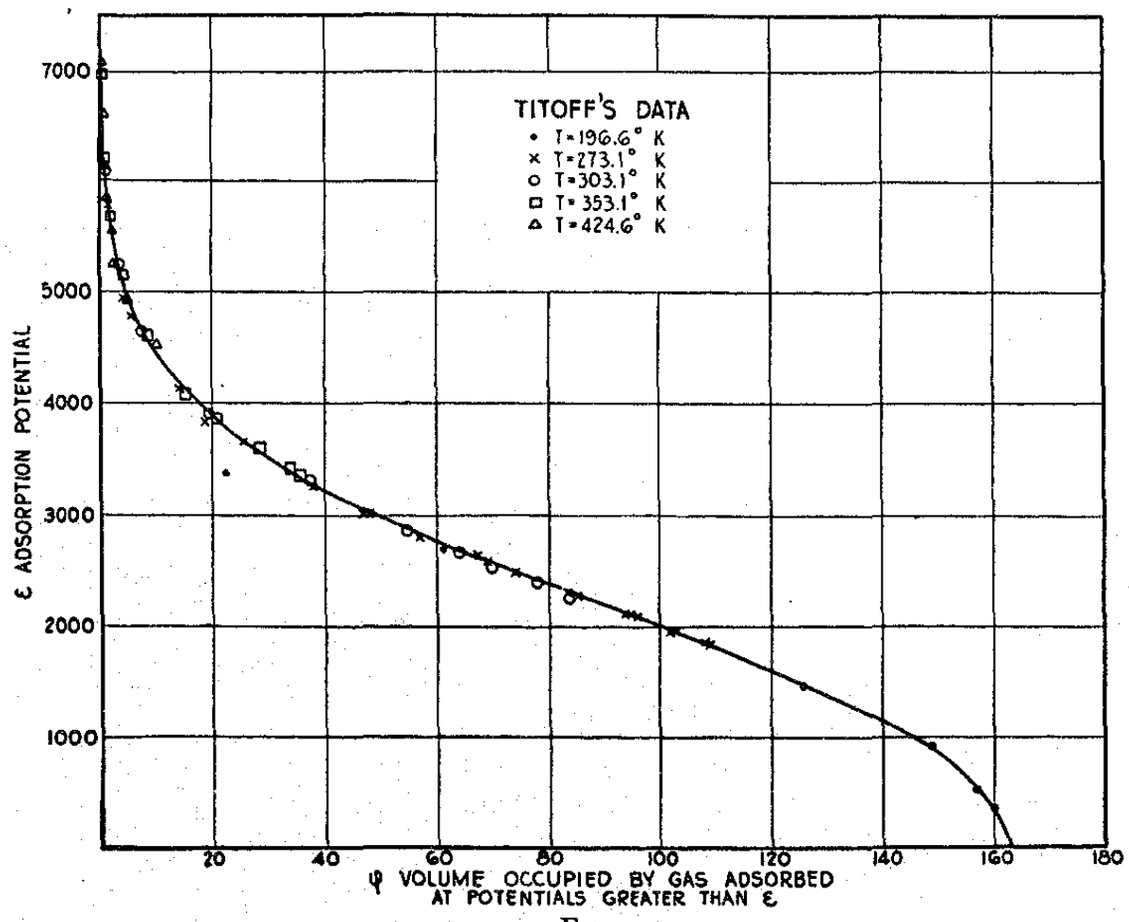

TITOFF'S DATA
• T=196.6° K
× T=273.1° K
○ T=303.1° K
□ T=353.1° K
△ T=424.6° K
ε ADSORPTION POTENTIAL
7000
5000
4000
3000
2000
1000
20
40
60
80
100
120
140
160
180
φ VOLUME OCCUPIED BY GAS ADSORBED AT POTENTIALS GREATER THAN ε

FIG. 2

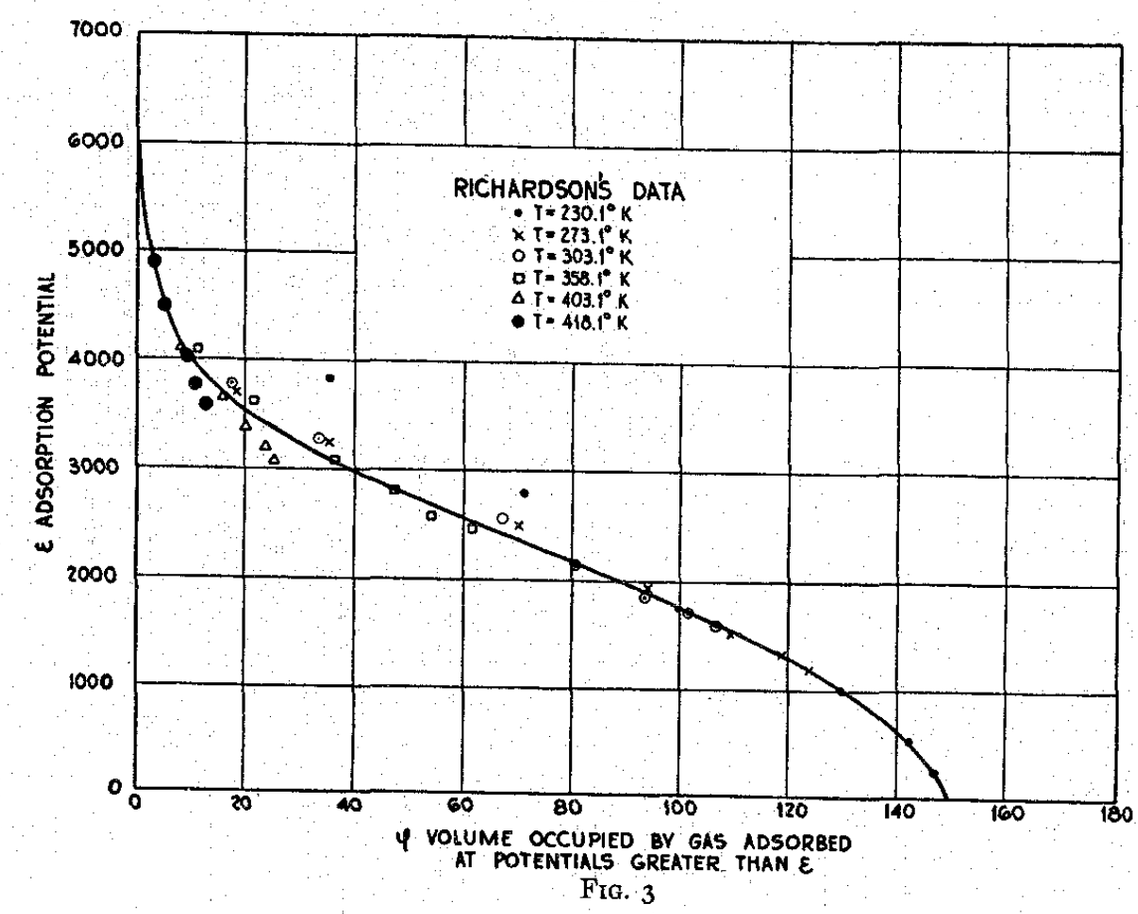

RICHARDSON'S DATA
• T=230.1° K
× T=273.1° K
○ T=303.1° K
□ T=358.1° K
△ T=403.1° K
● T=418.1° K
ε ADSORPTION POTENTIAL
7000
6000
5000
4000
3000
2000
1000
0
0
20
40
60
80
100
120
140
160
180
φ VOLUME OCCUPIED BY GAS ADSORBED AT POTENTIALS GREATER THAN ε

FIG. 3

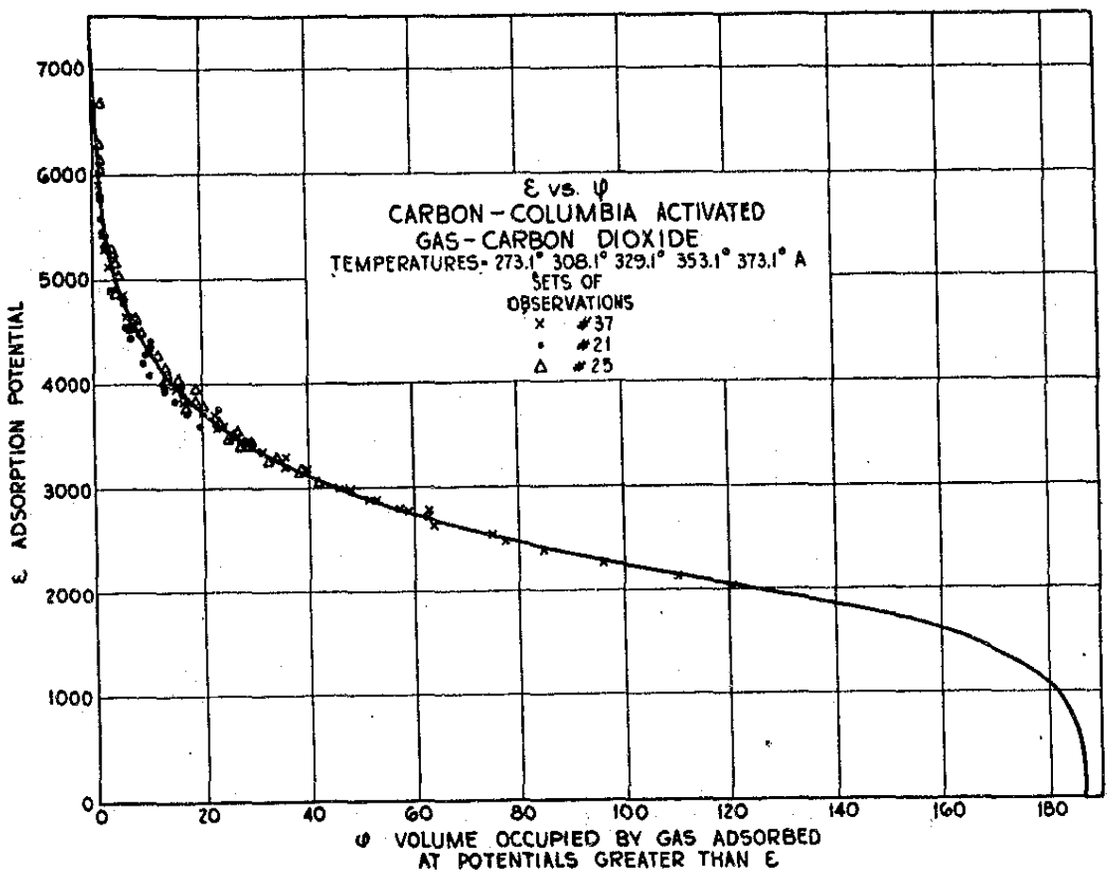

ε vs. φ
CARBON – COLUMBIA ACTIVATED
GAS – CARBON DIOXIDE
TEMPERATURES- 273.1° 308.1° 329.1° 353.1° 373.1° A
SETS OF
OBSERVATIONS
× #37
• #21
Δ #25
ε ADSORPTION POTENTIAL
φ VOLUME OCCUPIED BY GAS ADSORBED
AT POTENTIALS GREATER THAN ε
0
1000
2000
3000
4000
5000
6000
7000
0
20
40
60
80
100
120
140
160
180

FIG. 4

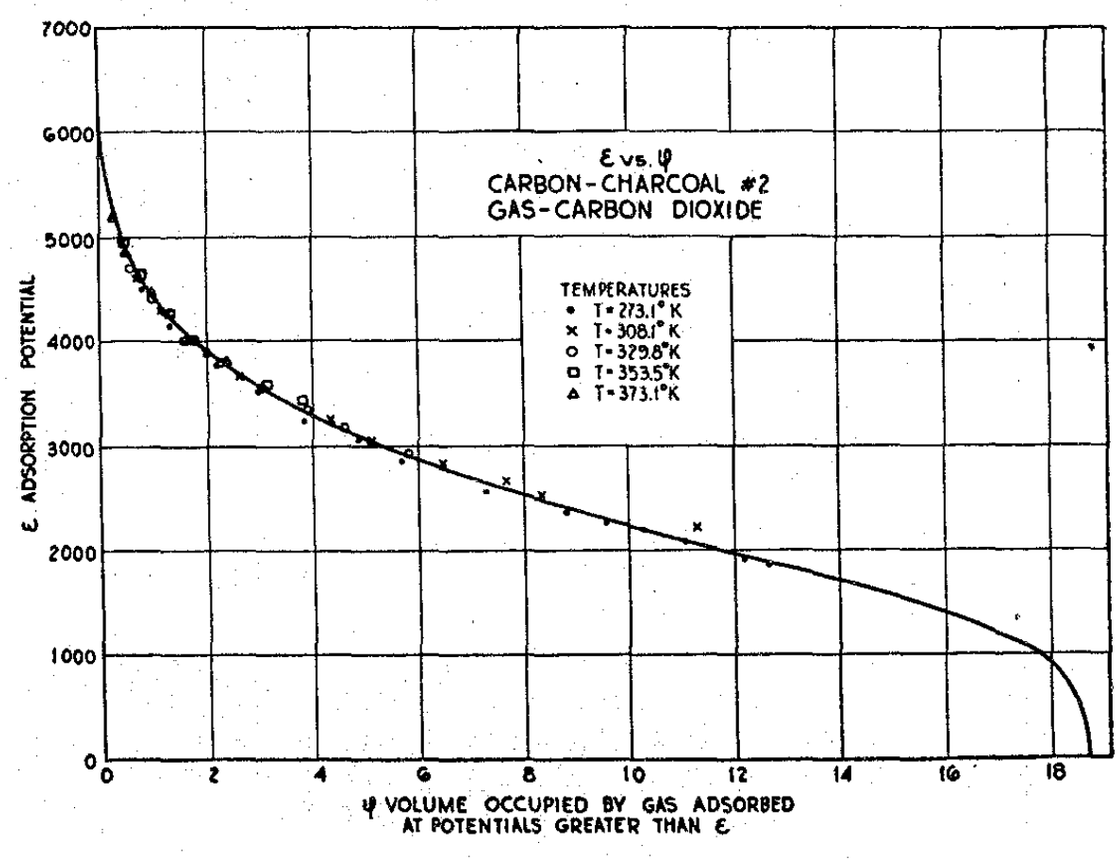

ε vs. φ
CARBON – CHARCOAL #2
GAS – CARBON DIOXIDE
TEMPERATURES
• T = 273.1° K
× T = 308.1° K
○ T = 329.8° K
□ T = 353.5° K
Δ T = 373.1° K
ε ADSORPTION POTENTIAL
φ VOLUME OCCUPIED BY GAS ADSORBED
AT POTENTIALS GREATER THAN ε
0
1000
2000
3000
4000
5000
6000
7000
0
2
4
6
8
10
12
14
16
18

FIG. 5

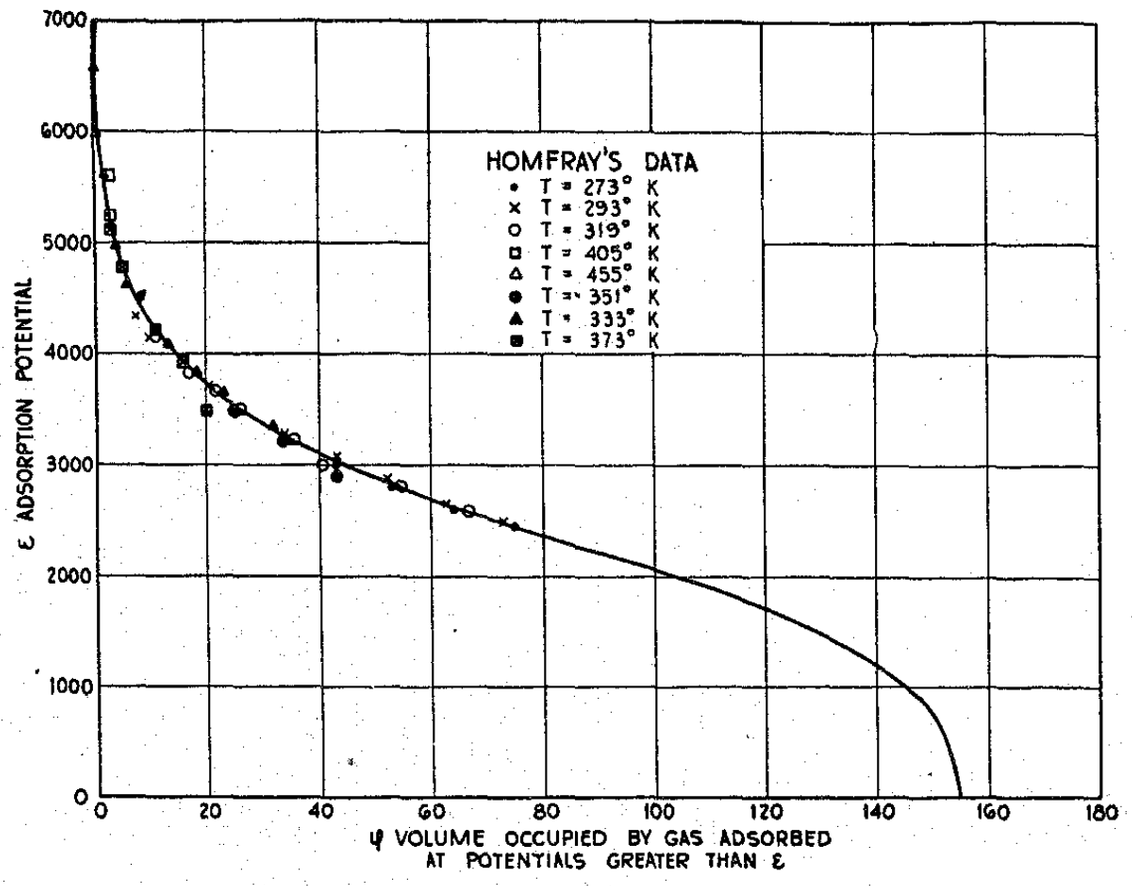

HOMFRAY'S DATA
• T = 273° K
× T = 293° K
○ T = 319° K
□ T = 405° K
△ T = 455° K
● T = 351° K
▲ T = 333° K
■ T = 373° K
ε ADSORPTION POTENTIAL
ψ VOLUME OCCUPIED BY GAS ADSORBED AT POTENTIALS GREATER THAN ε
0
1000
2000
3000
4000
5000
6000
7000
0
20
40
60
80
100
120
140
160
180

FIG. 6

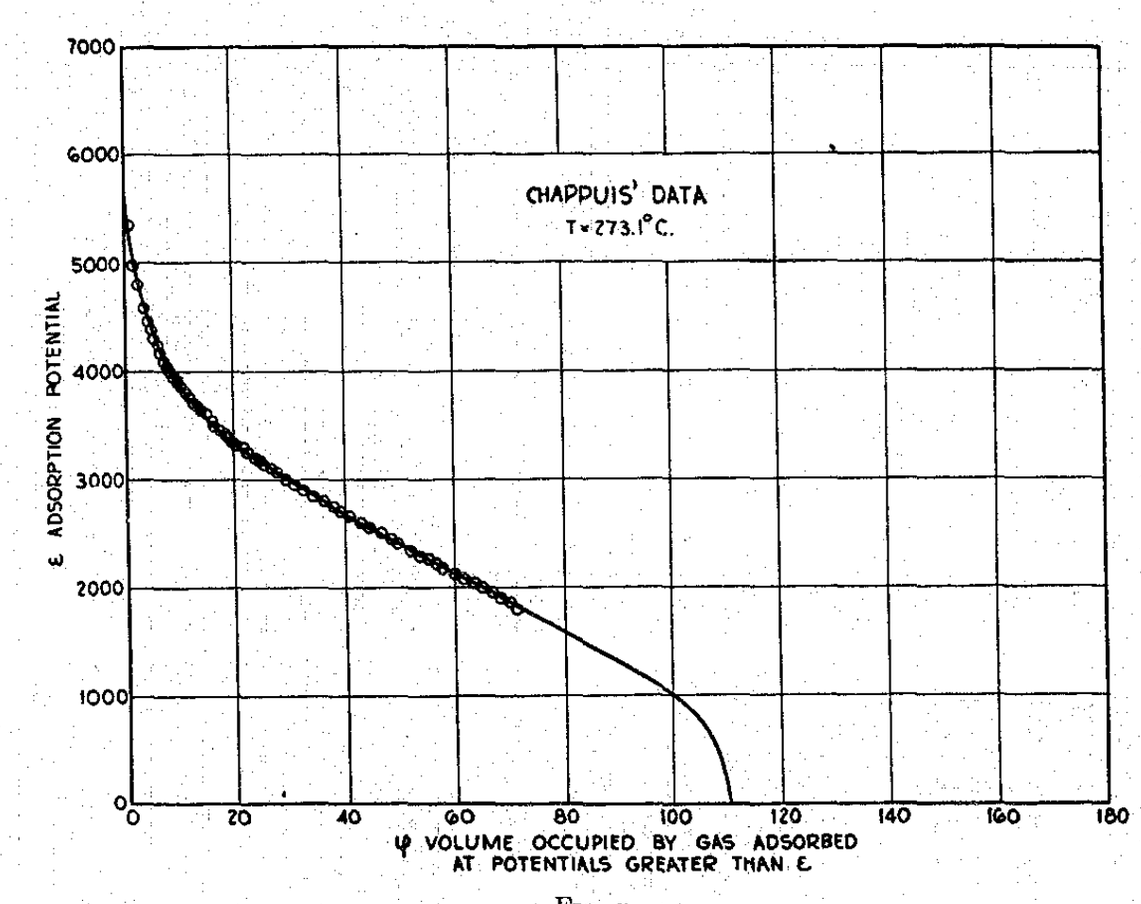

CHAPPUIS' DATA
T=273.1°C.
ε ADSORPTION POTENTIAL
ψ VOLUME OCCUPIED BY GAS ADSORBED AT POTENTIALS GREATER THAN ε
0
1000
2000
3000
4000
5000
6000
7000
0
20
40
60
80
100
120
140
160
180

FIG. 7

For instance, to calculate the value of ϵ_s for 373.1°,

$$\log \frac{72.9}{P} = 2.89 \left(\frac{304.1}{373.1} - 1 \right) = -0.5345,$$

or

$$\frac{72.9}{P} = 0.2921,$$

and

$$P = 249.57.$$

Then by successive approximations, using equation (9), $v_s = 3.323 \times 10^{-3}$, $\delta_s = 0.591$, and from the $\epsilon - \delta$ curve for this temperature the value of ϵ corresponding to a density of 0.591 is 3505, or $\epsilon_s = 3505$ as shown in Table I.

In Table II are given the corrections, $\Delta\epsilon$, obtained from equation (18), corresponding to the actual pressures used in the experiment. With these, corrected values of ϵ_s are obtained.

TABLE II

Calculation of ϵ_s

T = 196.6°K. Data of A. Titoff

P_x cm Hg	V_{δ_x}	$\Delta\epsilon$	ϵ_s cal
0.03	1824	2934	3384
0.18	304.0	2234	2684
4.13	13.25	1010	1460
16.86	3.245	460	910
48.31	1.133	49	499
69.10	0.7918	−91	359

T = 373.1°K. Data of S. O. Morgan

3.26	31.85	2567	6072
11.63	8.926	1623	5128
22.35	4.643	1139	4644
37.66	2.754	751	4256
54.85	1.890	472	3977
77.03	1.345	220	3725

T = 273.1°K. Data of S. O. Morgan

P_x	V_{δ_x}	$\Delta\epsilon$	ϵ_s
0.05	1520	3977	5797
0.33	230.3	2953	4773
0.92	82.61	2396	4216
1.94	39.18	1991	3811
3.02	25.23	1752	3572
4.65	16.34	1516	3336
6.07	12.52	1372	3192
7.62	9.974	1248	3068
10.58	7.183	1070	2890
13.33	5.701	944	2764
14.44	5.263	901	2721
17.15	4.431	806	2626
23.15	3.283	644	2464
27.25	2.789	556	2376
33.50	2.269	443	2263
43.33	1.754	303	2123
51.05	1.489	214	2034

Typical calculations of x and φ_s are given in Table III. In these, use is made of a temporary $\epsilon - \varphi$ curve obtained by equation (6) from data taken at a temperature well below the critical temperature. Values of ϵ and δ are obtained from Table I. To find ϵ_i, ϵ is corrected by $\Delta\epsilon$ form Table II. Then, φ_i is obtained from the $\epsilon - \varphi$ curve at the given values of ϵ_i. Equation (5) is used to determine the values of $x_{cal.}$ and x_s. These are compared with $x_{obs.}$ and $x_{corr.}$ obtained by use of equation (8). A corrected value of the density is obtained by equation (7) and a new value of φ_s by equation (6).

TABLE III

Calculation of x and φ_s

P_x	T	δ_i	ϵ	$\epsilon_i = \epsilon + \Delta\epsilon$	φ_i	$\varphi_1 - \varphi_2$	$\frac{\sigma_1 - \sigma_2}{2}$	Δx mg	
			0	1010	145.4				
4.13	196.6°	.0055	450	1460	125.6	19.8	.0028	.05544	
		1.25	450	1460	125.6	0			
		1.3	884	1894	103.0	22.6	1.275	28.82	
		1.4	2233	3243	29.6	73.4	1.35	99.09	
		1.5	5094	6104	1.4	28.2	1.45	40.89	= 170.92
		1.525		7250	0	1.4	1.513	2.118	= x_s

$$x_{cal.} = \Sigma\Delta x = 170.97$$

$$x_{obs.} = 171.5$$

$$x_{corr.} = \frac{171.5 \times 170.92}{170.97} = 171.4$$

$$\delta_s = \frac{170.92}{125.6} = 1.3608$$

$$\varphi_{corr.} = 171.4 \div 1.3608 = 126.0$$

3.26	373.1°	0	2567	73			
		.001	220	2787	57	16	.0005	.0080
		.004	600	3167	37.7	19.3	.0025	.0483
		.007	710	3277	33.5	4.2	.0055	.0231
		.010	1193	3760	19.2	14.3	.0085	.1215
		.030	1905	4472	7.9	11.3	.0200	.2260
		.050	2312	4879	4.5	3.4	.0400	.1360
		.080	2607	5174	3.1	1.4	.0650	.0910
		.100	2737	5304	2.7	.4	.0900	.0360
		.300	3243	5810	1.7	1.0	.2000	.2000
		.500	3417	5984	1.5	.2	.4000	.0800
		.591	3505	6072	1.3	.2	.5455	.1091
		.700	3634	6201	1.2	.1	.6455	.0646
		.900	4112	6679	.8	.4	.8000	.3200
		1.000	4566	7133	.3	.5	.9500	.4750
		1.032		7250	0	.3	1.0160	.3048

$x_{cal.}$	$x_{obs.}$	x_s	$x_{corr.}$	δ_s	φ
2.2434	2.2516	1.1644	1.1681	.89569	1.3

In Table IV a number of calculations of φ_s have been summarized. This includes the recalculation of φ_s after the temporary $\epsilon - \varphi$ curve has been replaced by a first approximation. The values of P_x are those given for this temperature in Table II.

TABLE IV

Calculation of φ_s by Successive Approximations

		1st Approximation			2nd Approximation					
	ϵ_s	$x_{obs.}$	δ' Assumed	φ_s'	φ_s''	$x_{cal.}$	$x_{s\ cal.}$	$x_{corr.}$	$\delta_{corr.}$	φ
273.1	5797	2.532	1.183	2.1	2.2	2.840	2.509	2.237	1.140	2.0
	4773	7.435		6.3	6.0	7.283	6.887	7.031	1.148	6.1
	4216	12.90		10.9	10.1	12.90	11.71	11.71	1.159	10.1
	3811	20.16		17.0	17.0	20.58	19.35	18.95	1.136	16.7
	3572	27.42		23.2	23.2	27.78	26.27	25.92	1.132	22.9
	3336	37.82		32.0	32.0	38.20	35.80	35.43	1.119	31.7
	3192	41.59		35.2	35.2	42.36	39.81	39.09	1.131	34.6
	3068	47.76		40.4	40.0	48.62	45.31	44.54	1.133	39.3
	2890	59.30		50.1	50.0	58.89	55.72	56.11	1.114	50.4
	2764	66.66		56.3	57.0	64.41	60.98	63.15	1.070	59.0
	2721	70.97		60.0	59.5	67.37	63.96	67.42	1.075	62.7
	2626	76.70		64.8	65.0	78.49	74.93	73.23	1.153	63.5
	2464	91.37		77.2	76.0	89.83	86.22	87.73	1.134	77.3
	2376	99.83		84.4	84.0	98.84	95.42	96.37	1.136	84.8
	2263	111.8		94.5	95.0	110.9	107.1	107.7	1.128	95.6
	2123	128.1		108.3	109.0	126.9	124.0	125.2	1.138	110.0
	2034	139.8		118.1	118.0	137.2	134.5	137.0	1.140	120.1

In accordance with the procedure outlined in the preceding paragraphs, $\epsilon - \varphi$ curves have been determined from the data of Homfray[13a], Titoff,[13] Richardson,[14] and Chappuis,[15] and from more recent data on two widely different types of charcoal ("Columbia Activated" and "Charcoal No. 2") which were obtained in these laboratories by S. O. Morgan using a novel method described in a previous article.[16] These curves are given together with the observed points in Figs. 2-7. In these figures the solid line has been drawn by the method of running averages. The fact that values of $\epsilon - \varphi$ calculated from the experimental data all fall on a single curve independent of the temperature justifies the assumption that the force of attraction of charcoal for carbon dioxide is not dependent on the temperature over the range considered.

In Table V are given the experimental data used in these calculations together with values of $x_{cal.}$ which have been obtained by use of the $\epsilon - \varphi$ curves. Examination of this table will show that in general there is very good agreement between $x_{obs.}$ and $x_{cal.}$ The average difference between the observed and calculated values being: Titoff, 4.53%; Richardson, 11.25%; Morgan on "Columbia Activated Charcoal," 3.17%, and on Charcoal No. 2, 2.48%; Homfray, 5.85%; and Chappuis, 1.29%. In general, the agreement is closest where the experimental accuracy is greatest. The excellent fit obtained for the data of Chappuis is probably due in part to the fact that the measurements were all made at 273.1°K. Furthermore, at least a part of the difference between the values obtained from Morgan's data on the two charcoals may be attributed to the fact that the data on Charcoal No. 2 were secured on a single sample, and that for "Columbia Activated Charcoal" include independent measurements made on three samples of the charcoal while the calculated values were obtained from the $\epsilon - \varphi$ curve determined from the data of Run No. 37 alone. The average deviations of the different runs on Columbia Activated Charcoal are: No. 21, 4.74%; No. 25, 2.59%; and No. 37, 2.18%. It is interesting to note that the deviation for Charcoal No. 2 and the "Columbia" Charcoal are so nearly identical, in spite of the fact that the adsorptive capacity of the first is only approximately one-tenth that of the second. The agreement obtained in the remaining cases is in the same order as obtained by Berenyi, although by using the method of calculation described in this paper the average differences between experimental and calculated values are not so great as those given in his paper; i.e., for Titoff, 4.53% against Berenyi's 7.16%; Homfray 5.85% vs. 12.47%; and Richardson 11.25% vs. 15.7%. A part of the better agreement obtained by the method of calculation proposed in this paper is undoubtedly due to the establishment of a better $\epsilon - \varphi$ curve. Berenyi used an $\epsilon - \varphi$ curve determined from the 273.1°K isotherm and an arbitrary completion of the curve to $\varphi_{max.}$ The calculations made in this paper show, therefore, that the ad-

[13] A. Titoff: Z. physik. Chem., **74**, 662 (1910).
[14] L. B. Richardson: J. Am. Chem. Soc., **39**, 1842 (1917).
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TABLE V
Calculated and Observed Values of x

A. Data of A. Titoff.

T = 196.6°K.

P_x	x_{obs}	x_{cal}
0.03	30.17	45.79
0.18	82.05	81.59
4.13	171.1	171.0
16.86	205.8	205.4
48.31	220.5	220.6
69.10	225.6	224.6

T = 273.1°K.

0.05	1.679	1.697
0.32	6.840	6.165
1.09	16.81	15.28
2.54	29.94	27.75
8.30	54.92	55.10
17.35	78.87	79.00
31.59	99.32	101.73
45.72	112.32	114.71
58.91	121.32	124.44
70.32	127.56	130.67
75.51	130.18	134.16
0.24	4.661	4.833
1.77	22.32	21.64
8.59	56.21	55.17
18.94	80.98	82.36

T = 273.1°K. cont.

P_x	x_{obs}	x_{cal}
33.53	100.82	103.93
45.26	111.94	115.03
0.22	4.519	4.639
1.87	22.36	22.11
5.51	44.59	43.88
12.21	66.06	66.90
22.93	86.79	89.54
33.77	100.52	103.40
47.13	113.55	116.04
60.55	121.85	125.49
73.09	128.71	132.45

T = 303.1°K.

0.13	1.002	1.114
0.53	3.604	3.554
1.47	7.931	7.684
5.07	20.35	19.22
13.85	38.98	37.56
28.33	57.07	57.15
39.89	67.35	68.00
49.81	72.40	74.68
62.18	81.93	84.04
75.86	88.83	91.89

T = 353.1°K.

P_x	x_{obs}	x_{cal}
0.43	0.554	05.90
1.25	1.500	16.58
2.66	3.042	3.251
5.44	5.900	6.002
12.09	11.54	11.36
23.04	18.86	18.30
35.64	25.84	25.67
52.03	33.73	32.80
66.92	38.86	38.19
73.99	41.31	40.72

T = 424.6°K.

1.61	0.289	0.298
3.66	0.747	0.744
6.81	1.423	1.466
10.48	2.163	2.254
15.45	3.173	3.143
22.27	4.470	4.504
31.94	6.235	6.585
44.75	8.401	8.743
52.52	11.42	11.00
62.91	13.03	12.84
74.79	14.75	13.63

TABLE V (Continued)

B. Data of L. B. Richardson

T = 230.1°K.

P_x	x_{obs}	x_{cal}
0.6	43.06	14.94
3.2	86.39	59.48
16.6	124.9	125.2
56.0	167.0	165.1
117.9	186.2	184.4
182.4	194.7	192.6

T = 273.1°K.

2.4	22.54	18.10
5.4	41.91	32.25
22.6	81.64	76.02
62.6	111.1	110.1
135.7	132.1	132.7
191.3	144.5	142.9
245.0	149.6	149.5

T = 303.1°K.

P_x	x_{obs}	x_{ca}
7.3	21.55	16.53
16.8	39.34	31.24
56.3	71.96	66.63
111.7	89.15	91.71
183.0	105.6	109.4
223.8	115.4	115.9
281.5	122.2	123.1

T = 358.1°K.

29.2	16.41	12.93
58.1	29.65	22.85
124.4	44.28	41.46
184.0	52.19	53.29
249.5	57.13	63.44
293.5	65.04	69.50

T = 403.1°K.

P_x	x_{obs}	x_{cal}
52.1	10.08	10.07
88.6	16.80	15.89
159.8	25.90	26.72
219.7	28.86	33.31
281.1	32.02	40.32
323.7	32.36	44.47

T = 418.1°K.

59.2	8.11	8.77
97.1	13.64	13.61
168.8	20.95	21.94
229.0	21.94	28.13
290.1	24.61	34.04

TABLE V (Continued)

C. Data of S. O. Morgan on "Columbia Activated" Charcoal

T = 273.1°K.
Run No. 21

P_x	x_{obs}	x_{cal}
0.13	3.661	3.357
0.63	8.625	8.700
1.19	13.15	13.43
1.91	18.73	18.69
2.84	24.33	24.72

Run No. 25

0.01	2.243	2.094
0.20	5.616	5.891
0.56	10.22	10.81
1.09	15.32	15.42
1.71	20.14	20.37
2.42	24.87	23.74
3.53	30.26	29.72
4.16	34.04	33.71
4.51	37.86	38.92
5.73	43.94	45.29
7.94	49.89	51.09

Run No. 37

0.05	2.532	2.604
0.33	7.435	7.332
0.92	12.90	13.33
1.94	20.16	20.62
3.02	27.42	27.22
4.65	37.82	36.08
6.07	41.59	42.65
7.62	47.76	48.62
10.58	59.30	58.89

T = 273.1°K (Cont.)
Run No. 37 cont.

P_x	x_{obs}	x_{cal}
13.33	66.66	64.41
14.44	70.97	67.37
17.15	76.70	78.49
23.15	91.37	89.93
27.25	99.83	98.84
33.50	111.8	110.9
43.33	128.1	126.9
51.05	139.8	137.2

T = 308.1°K.
Run No. 21

0.80	3.608	3.760
2.67	8.461	8.975
4.71	12.87	14.05
7.48	18.27	19.07
10.80	23.68	24.72

Run No. 25

0.25	2.216	2.189
1.02	5.535	5.693
2.58	10.01	10.37
4.66	14.94	15.32
6.89	19.62	20.85
9.79	24.12	25.65
13.19	29.26	31.43
15.74	32.87	33.69
18.40	36.43	36.96
22.80	42.22	43.16
27.22	47.94	48.44

T = 308.1°K. (Cont.)
Run No. 37

P_x	x_{obs}	x_{cal}
0.35	2.503	2.707
1.77	7.288	7.865
3.83	12.60	13.51
7.27	19.63	20.54
16.75	34.63	35.15
21.20	40.13	40.90
26.37	45.92	45.80
35.29	56.87	56.21
44.12	63.65	63.78
48.33	67.61	67.49
54.73	73.00	74.26
72.82	86.54	87.15

T = 329.8°K.
Run No. 21

1.75	3.535	3.920
5.15	8.277	8.761
8.80	12.56	12.97
14.15	17.77	18.14
19.84	23.03	23.07

Run No. 25

0.60	2.182	1.713
2.29	5.411	4.320
5.26	9.761	9.660
9.15	14.53	14.73
13.14	19.03	19.17
17.90	23.37	23.90
23.64	28.29	28.47
27.74	31.77	31.65
32.31	35.15	34.84
40.22	40.60	40.33
48.40	45.98	45.48

TABLE V (Continued)

T = 329.8°K (cont.)
Run No. 37

P_x	x_{obs}	x_{cal}
0.89	2.451	2.394
3.70	7.111	7.010
7.62	12.25	12.62
14.16	19.02	20.13
20.83	25.74	24.84
30.64	33.39	33.46
38.05	38.61	38.98
46.70	44.08	45.11
62.95	54.36	54.27
75.55	60.83	61.81

T = 353.5°K

Run No. 21

3.70	3.380	3.697
9.84	7.943	3.477
16.28	12.14	12.80
24.88	17.02	17.84
34.46	21.98	22.72

Run No. 25

1.39	2.111	2.242
4.70	5.197	5.405
10.20	9.323	9.160
16.97	13.83	13.53

T = 353.5°K (cont.)
Run No. 25 cont.

P_x	x_{obs}	x_{cal}
23.79	18.08	17.79
31.64	22.14	22.21
41.42	26.75	26.85
48.69	29.91	30.21
57.04	32.97	33.23
67.82	38.21	37.52

Run No. 37

1.93	2.360	2.448
8.27	6.711	6.616
14.33	11.68	11.56
25.26	18.07	18.13
52.75	31.51	31.57
63.85	36.37	36.93
78.45	41.39	42.36

T = 373.1°K

Run No. 21

6.13	3.230	3.394
15.87	7.534	7.875
26.21	11.36	12.26
37.53	16.19	16.59
53.44	20.74	22.13

T = 373.1°K (cont.)
Run No. 25

P_x	x_{obs}	x_{cal}
2.42	2.024	1.798
7.67	4.944	4.935
15.99	8.836	8.392
25.96	13.09	13.55
37.29	16.96	17.17
47.61	20.82	20.71
62.61	24.99	25.49
70.19	28.17	27.85

Run No. 37

3.26	2.252	2.243
11.63	6.444	6.559
22.35	11.03	11.23
37.66	17.06	17.18
54.85	22.93	23.33
77.03	29.57	30.21

TABLE V (Continued)

D. Data of S. O. Morgan on Charcoal No. 2

T = 273.1°K

P_x	x_{obs}	x_{cal}
0.54	0.992	0.987
1.04	1.597	1.597
2.10	2.619	2.604
3.30	3.513	3.463
5.54	4.566	4.685
7.70	5.751	5.572
11.52	6.765	6.760
19.50	8.649	8.771
28.28	10.44	10.52
34.58	11.30	11.59
37.75	12.00	12.05
46.85	13.08	13.25
63.48	14.38	14.74
71.83	15.00	15.34

T = 308.1°K

P_x	x_{obs}	x_{cal}
2.50	0.903	0.954
4.18	1.459	1.453
7.93	2.360	2.295
11.54	3.149	3.071
23.10	5.080	4.904
31.38	5.907	5.881
48.53	7.410	7.503
65.13	8.876	8.776
74.78	9.619	9.509

T = 329.8°K

P_x	x_{obs}	x_{cal}
4.70	0.814	0.839
7.22	1.336	1.245
13.62	2.131	2.094
19.31	2.837	2.740
27.63	3.637	3.538
36.95	4.529	4.328
47.36	5.288	5.079
69.03	6.620	6.429

T = 329.8°K (cont.)

P_x	x_{obs}	x_{cal}
7.68	0.704	0.705
11.86	1.160	1.119
21.28	1.846	1.814
29.39	2.468	2.368
53.55	3.928	3.785
65.88	4.626	4.366

T = 353.5°K

P_x	x_{obs}	x_{cal}
10.45	0.607	0.683
16.44	1.001	1.011
28.12	1.619	1.539
38.80	2.143	2.046
53.93	2.718	2.661
69.08	3.402	3.209

T = 373.1°K

TABLE V (*Continued*)

E. Data of I. F. Homfray

T = 273.1°K

P_x	x_{obs}	x_{cal}
6.0	41.37	43.39
8.7	51.54	51.51
12.3	62.92	61.93
17.9	75.45	75.13
24.2	87.63	88.00

T = 293°K

2.0	9.489	10.30
2.9	12.85	13.29
6.3	25.05	24.94
8.5	30.58	30.90
12.8	41.06	40.53
18.6	51.06	50.84
25.8	62.27	60.95
37.4	74.59	74.71
50.0	86.45	86.35

T = 319°K

7.0	12.65	13.56
12.1	18.58	20.19
15.1	24.65	24.46

T = 319°K (cont.)

P_x	x_{obs}	x_{cal}
20.0	30.11	29.43
30.5	40.33	38.58
43.6	49.95	51.02
59.7	60.75	59.51
84.2	72.49	71.30

T = 333°K

30.4	29.65	30.56
47.5	39.60	41.55
72.6	48.69	54.31

T = 351°K

7.2	6.187	5.937
11.7	9.093	9.244
17.6	12.26	11.43
25.5	17.99	17.05
36.5	23.78	22.47
47.9	29.00	27.22
72.6	38.55	36.05

T = 373.1°K

P_x	x_{obs}	x_{ca}
6.1	3.163	3.305
12.1	5.990	6.116
18.8	8.836	9.214
27.2	11.86	12.57
42.1	17.40	17.58
60.6	22.87	23.41
76.7	27.93	27.84

T = 405°K

49.2	11.13	8.38
76.8	16.27	11.75

T = 455°K

25.1	2.570	3.58
48.8	4.883	6.21
73.6	7.117	7.82

TABLE V (Continued)

F. Data of Chappuis $T = 273.1°$

P_x	x_{obs}	x_{cal}	P_x	x_{obs}	x_{cal}	P_x	x_{obs}	x_{ca}
0.113	0.759	0.735	2.822	16.58	16.15	12.63	41.79	41.73
0.223	1.704	1.604	2.998	17.29	17.43	13.80	43.77	43.42
0.305	2.469	2.633	3.175	18.02	17.96	15.14	45.80	46.10
0.470	3.829	3.723	3.392	18.75	18.93	16.58	47.86	47.53
0.580	4.468	4.477	3.548	19.47	19.61	18.05	49.85	49.68
0.670	5.225	5.151	3.755	20.22	19.80	19.67	51.87	51.91
0.780	5.942	6.038	3.975	21.03	21.02	21.57	54.03	53.92
0.905	6.624	6.718	4.194	21.82	22.05	23.67	56.26	56.30
0.986	7.302	7.356	4.427	22.59	22.70	25.81	58.39	58.73
1.100	7.990	7.810	4.693	23.56	23.51	28.17	60.53	60.58
1.240	8.714	8.600	5.078	24.79	24.81	30.84	62.68	62.86
1.352	9.408	9.369	5.463	25.98	25.74	33.50	64.84	64.85
1.495	10.14	10.44	5.984	27.50	27.39	36.47	66.91	66.84
1.625	10.84	10.88	6.413	28.56	28.80	39.68	69.05	69.32
1.762	11.54	11.87	6.567	28.96	29.20	43.05	71.03	70.71
1.882	12.24	11.98	7.010	30.09	30.59	46.49	73.00	72.58
2.012	12.94	12.59	7.712	31.83	31.26	50.36	75.00	74.69
2.170	13.66	13.30	8.548	33.74	33.91	54.31	76.94	76.86
2.312	14.39	14.23	9.437	35.70	35.76	59.20	78.87	79.51
2.494	15.13	14.96	10.41	37.72	36.98	64.64	80.93	82.11
2.641	15.85	15.79	11.51	39.77	39.78	70.34	82.79	84.37
						76.34	84.67	86.83

sorption of a gas at any temperature and pressure by a given adsorbent may be quite accurately estimated if the distribution of potential with volume ($\epsilon - \varphi$) for the gas and adsorbent is first determined. By similar calculations on the adsorption of nitrogen, hydrogen, helium, neon, and argon,—the data having already been obtained by S. O. Morgan—we hope to be able to establish a relationship between the adsorption of a gas and certain other properties.

We wish to take this opportunity to acknowledge the excellent assistance of Mr. S. O. Morgan in securing the adsorption data and of Misses J. V. Glenn and A. E. Hamilton in making the necessary computations and preparing the figures for this paper.

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Lo-427

STUDIES ON THE HYDROLYSIS OF COMPOUNDS WHICH MAY OCCUR IN PORTLAND CEMENT[1]

BY WM. LERCH AND R. H. BOGUE

The reactions occurring when portland cement is gauged with water are complicated because of the presence of a number of constituent compounds, each of which undergoes chemical change by interaction with water. These reactions are involved in the processes of setting and hardening.

Hydrolysis and hydration both assume important roles in these processes. A given compound of portland cement may interact with water by the process of hydrolysis or by the process of hydration, or both, but the rate with which these reactions proceed in the case of any compound appears to be dependent on several factors.

Inasmuch as the value of a cement in a mortar or concrete seems to be concerned with the rate with which these reactions proceed, and the nature and amount of the end products formed, it becomes imperative that we understand these processes and conditions of equilibrium if the greatest advantage is to be taken of the possible means for controlling them.

In the development of an orderly program for the study of these reactions, it is necessary to differentiate between hydrolysis and hydration and to study each separately. Otherwise the underlying causes of the several reactions are not entirely clear. It is also necessary to investigate first the pure constituent compounds of cement and to determine their behavior under conditions that are made arbitrarily ideal. There is no immediate relation between these conditions and those of cement practice but the former must be determined before the latter can be sufficiently explained. It should be borne in mind however that it is not permissible to assume that, because *e. g.* tricalcium silicate hydrolyzes to monocalcium silicate hydrate in a given time in a certain large amount of water, it also will proceed to the same point in the same time when present in the concentrated solutions from freshly mixed concretes and in the presence of the many soluble substances of the wet mixture. This report is a preliminary survey concerned only with pure cement compounds and not at all with commercial portland cement.

There are considered:

(1) The equilibria conditions in the reactions of hydrolysis.

(2) the rate with which these reactions proceed under various concentrations of hydroxyl ion, and

(3) the nature of the end products resulting under the several conditions imposed.

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These have been studied independently with each of several compounds which have been reported to exist in portland cement clinker.

Preliminary Discussion

Since the terms "hydrolysis" and "hydration" are sometimes used interchangeably, it is desirable to define each. By *hydrolysis* is meant such reactions of a compound (salt type) with water that a part or all of the compound becomes decomposed either completely into the corresponding acid and base or incompletely, forming an acid or basic salt or a derivative of the same. Thus the complete hydrolysis of $_3CaO.Al_2O_3$ would give:

$$_3CaO.Al_2O_3 + xH_2O \rightleftarrows {}_3Ca(OH)_2 + Al_2O_3.aq.$$

The partial hydrolysis of $_3CaO.SiO_2$ could give:

$$_3CaO.SiO_2 + xH_2O \rightleftarrows CaO.SiO_2.aq. + {}_2Ca(OH)_2.$$

By *hydration* is meant the direct addition of the elements of water as:

$$CaO + H_2O \rightleftarrows Ca(OH)_2$$

or

$$_3CaO.Al_2O_3 + xH_2O \rightleftarrows {}_3CaO.Al_2O_3.aq.$$

The reactions of hydrolysis are not to be considered as unique or different from those of the electrolytic dissociation of neutral salts except in the degree to which the dissociated ions of the salt combine with the $H^{\cdot}$ and the OH' ions of water to form undissociated acid or base. Indeed it has been suggested that the term hydrolysis might be omitted altogether since no break is required in the thermodynamic considerations of the equilibria, expressed in the Mass Law, which apply to the development of an excess of $H^{\cdot}$ or OH' ions as a result of the dissociation. The term however has found a distinct place in the literature and will be employed primarily to differentiate this type of reaction with the ions of water from the reactions of hydration.

The major constituents of cement are apparently compounds formed from weak acidic oxides,—silica, alumina, and ferric oxide,—and a relatively strong base, calcium oxide. Under the influence of water, such compounds would be expected to undergo hydrolysis with the formation of salts of lower basicity (or even, in the limiting case, of the free acidic components as hydrous silica, hydrous alumina or hydrous ferric oxide) and the free base, $Ca(OH)_2$.

Aqueous solutions of cement compounds are found to be alkaline in reaction. Since such reaction is determined by the ratio of the ionization constants and the concentrations of the respective $H^{\cdot}$ and OH' ions, it follows that $Ca(OH)_2$ possesses either a higher ionization constant than the acidic components, or that its concentration in solution is much greater, or both. In either case, hydrolysis has occurred, and in accordance with the mass law, will proceed until an equilibrium is established or until the available solvent is removed.

In order to make clear the ionic relations involved in the hydrolysis of cement compounds, the following hypothetical reactions are presented. These represent possible stages in the hydrolysis of $_3CaO.SiO_2$, and are offered only in an attempt to analyze previously obtained experimental data, and to furnish the premises for the present study.

1 $$3CaO.SiO_2 \rightleftarrows 3Ca^{\cdot\cdot} + SiO_5''''''$$
$$6H_2O \rightleftarrows 6OH' + 6H^{\cdot}$$
$$\uparrow\downarrow \qquad \uparrow\downarrow$$
$$3Ca(OH)_2 \quad H_6SiO_5$$
$$(SiO_2.aq.)$$

2. $$3CaO.SiO_2 \rightleftarrows Ca^{\cdot\cdot} + Ca_2SiO_5''$$
$$2H_2O \rightleftarrows 2OH' + 2H^{\cdot}$$
$$\uparrow\downarrow \qquad \uparrow\downarrow$$
$$Ca(OH)_2 \quad Ca_2SiO_4 + H_2O$$
$$(2CaO.SiO_2.aq.)$$

3. $$2CaO.SiO_2 \rightleftarrows Ca^{\cdot\cdot} + CaSiO_4''$$
$$2H_2O \rightleftarrows 2OH' + 2H^{\cdot}$$
$$\uparrow\downarrow \qquad \uparrow\downarrow$$
$$Ca(OH)_2 \quad CaSiO_3 + H_2O$$
$$(CaO.SiO_2.aq.)$$

4. $$CaO.SiO_2 \rightleftarrows Ca^{\cdot\cdot} + SiO_3''$$
$$2H_2O \rightleftarrows 2OH' + 2H^{\cdot}$$
$$\uparrow\downarrow \qquad \uparrow\downarrow$$
$$Ca(OH)_2 \quad H_2SiO_3$$
$$(SiO_2.aq.)$$

Equation No. 1 represents the several equilibria which would be expected to obtain under conditions where the $3CaO.SiO_2$ were caused to proceed towards complete hydrolysis. It is indicated in the report which follows. however, that intermediate products are formed, and that the hydrolysis will not go to completion unless the soluble $Ca(OH)_2$ is continuously removed. Equations 2, 3, and 4 represent possible stages in the hydrolysis wherein one, two and three mols, respectively, of CaO are removed. Reaction 3 would be expected to begin before the completion of reaction 2, and reaction 4 before the completion of reaction 3. Still other intermediate reactions are of course conceivable. Assuming, for the present, that the reactions as given represent the sum total of the hydrolysis reactions, a consideration of the mass law would require that each proceeded until its respective equlibrium condition were realized.

Thus, in reaction 2, $2CaO.SiO_2$ aq. is one of the products, and in reaction 3, this product is dissociated into $CaO.SiO_2$ aq. If $2CaO.SiO_2.aq.$ were the least soluble in any given set of conditions, or produced the lowest ion concentration (solubility product) of any of the products of dissociation, it would form in largest amount when the components represented were brought together. But if $CaO.SiO_2.aq.$ were less soluble, or produced a lower ion concentration under the conditions of the experiment, this would be formed in larger amount. Again, by reaction 4, the $CaO.SiO_2.aq.$ would be dissociated to $SiO_2.aq.$ if

the latter were the more insoluble or the least ionized under the given conditions. In each of these cases, however, the concentration of the Ca and OH ions determines the position of the equilibrium. This may be seen better by writing one of the reactions in a different form. Equation 4 may be written:

$$CaO.SiO_2.aq. + xH_2O \rightleftarrows Ca(OH)_2 + SiO_2.aq.$$

and since $\frac{[Ca(OH)_2] \times [SiO_2.aq.]}{[CaO.SiO_2.aq] \times [H_2O]} = k$, where k is the mass law constant, any increase in the $Ca(OH)_2$ in solution must result in a decrease in the SiO_2.aq. in solution and a consequent forcing of the reaction to the left, until the constant is restored to the original value, k.

From the above analysis of the hydrolysis reactions of $_3CaO.SiO_2$, it is apparent that the reaction product may conceivably consist of a combination of the several intermediate and end products mentioned (or perhaps others) and that the position of this equilibrium condition depends, among other factors, on the concentration of $Ca(OH)_2$ present. A corollary of this conclusion will indicate that if a sufficiently high concentration of $Ca(OH)_2$ is introduced at the start, it may serve almost completely to prevent the progress of the reaction, or even, in some cases, to reverse the hydrolysis. For example, $_2CaO.SiO_2$ might conceivably be caused to proceed to the production of the more basic $_3CaO.SiO_2$.

$$_2CaO.SiO_2 + Ca(OH)_2 \rightleftarrows {}_3CaO.SiO_2 + H_2O$$

In this case the $_2CaO.SiO_2$ would function as an acidic component.

It should be possible, in view of the above, to find a concentration of OH ion at which each of the cement compounds will be in equilibrium with the solution, provided this theoretical concentration is within the range of available values. If a basic solution is added to a solid portion of one of the compounds, and the pH of the solution is thereby raised, hydrolysis is taking place, the compound acting basic with respect to the solution. If, on adding a more basic solution, the pH is lowered as a result of the reaction, combination is taking place, the compound acting acidic. At some intermediate OH ion concentration, there will be neither hydrolysis nor combination. This is the equilibrium concentration.

The problem is further advanced by a study of the speed of the reactions under various concentrations of hydroxyl ion, and by a study of the nature of the intermediate and end products formed under these various conditions. These several problems constitute the subject of this report.

Preparation of the Cement Compounds

The compounds studied in this investigation are as follows:

5-3 calcium aluminate,	$_5CaO.{}_3Al_2O_3$,
Tricalcium aluminate,	$_3CaO.Al_2O_3$,
Gamma dicalcium silicate,	$\gamma_2CaO.SiO_2$,
Beta dicalcium silicate,	$\beta_2CaO.SiO_2$,
Tricalcium silicate,	$_3CaO.SiO_2$,
Dicalcium ferrite,	$_2CaO.Fe_2O_3$

Rankin[2] and Bates[3] state that these include the major constituents of a well-burned portland cement clinker, making up over 90 per cent of the product.

These compounds were prepared from calcium carbonate, alumina, silica, and ferric oxide of the composition given in Table I.

TABLE I
Compositions of Raw Materials[4]

	Calcium Carbonate	Alumina	Silica	Ferric Oxide
SiO_2	nil	0.01	98.75	0.25
Al_2O_3	0.08	98.48	0.61	—
Fe_2O_3	0.01	0.002	0.31	99.02
FeO	—	—	—	—
CaO	55.73	nil	0.30	0.20
MgO	0.01	—	—	—
Alkalies	0.04	—	—	—
SO_3	trace	—	—	trace
Cl	trace	—	—	—
CO_2	44.10	—	—	—
Loss on ignition	—	1.42	0.12	0.59

Calcium Aluminates.—The calcium aluminates were made by mixing calcium carbonate and alumina in the proper proportions with water and molding into sticks. These were then heated in an updraft, gas-fired kiln. The temperature was slowly raised to 1350°[5] and maintained at that temperature ± 20° for four hours. In each case the product was ground, molded, and heated a second time to insure homogeneity. On examination under the microscope[6] each of the calcium aluminates was found to be practically pure. They were found to contain no free lime by White's test,[7] or by the ammonium acetate titration method.[8]

Gamma Dicalcium Silicate.—Gamma dicalcium silicate was prepared by mixing calcium carbonate and silica in the proper proportions and molding with water into sticks. These were heated to 1500° and held at that temperature for about 2 hours. The gas was then turned off and the sticks removed from the furnace. These sticks, which were very hard at high temperatures, crumbled completely on cooling. This crumbling or "dusting" is due to the

[2] J. Ind. Eng. Chem., 3, 211 (1911).
[3] Concrete-Cement Age (C. M. S.) 2, 3 (1913).
[4] Analyses by H. C. Stecker.
[5] Temperatures thruout the paper are expressed in degrees Centigrade.
[6] All microscopic examinations were made by F. W. Ashton.
[7] A. H. White: J. Ind. Eng. Chem., 1, 5 (1909).
[8] *Cf.* Lerch and Bogue: Ind. Eng. Chem., 18, 739 (1926).

inversion of beta dicalcium silicate to the gamma form, with an accompanying increase in volume of about 10 per cent.[9] The product was of such fineness that 95 per cent passed a 100 sieve, and about 85 per cent passed a 200 sieve.

Beta Dicalcium Silicate.—In the preparation of beta dicalcium silicate, it was necessary to prevent the inversion of this compound to the gamma form, Bates and Klein[10] had found that the addition of small quantities of boric oxide or chromic oxide would entirely prevent this inversion of the dicalcium silicate to the gamma modification.

In the preparation of beta dicalcium silicate, 0.5 per cent of boric oxide was added to the mixture. The sticks, in this case, were heated to about 1500° and maintained at that temperature for about three hours. They were removed from the furnace while hot, and quenched in air, since rapid cooling is a further aid in the prevention of dusting. Examined under the microscope, the product was found to be practically pure beta dicalcium silicate.

Tricalcium Silicate.—A special procedure was necessary in the preparation of tricalcium silicate. It was found that when all of the calcium carbonate, required to give the proper composition, was added before the first heating, it was impossible to attain complete combination at the temperature obtainable (approximately 1550°). This may be due to the formation of crystals of high-burned lime before the latter enter into combination with the silica. These crystals, when once formed, are very inactive. In the method finally adopted,[11] the calcium carbonate was added in increments, and the mixture heated after each addition. The first composition was approximately 2.3 $CaO:1SiO_2$, the second $2.6CaO:1SiO_2$, the third $2.9CaO:1SiO_2$. This last product was then analyzed and the amount of calcium carbonate, necessary to bring the composition to that of tricalcium silicate, was added. Each mixture was heated to 1500°–1525° and maintained at that temperature for three hours. The final product examined under the microscope was found to be practically pure tricalcium silicate, with a trace of beta dicalcium silicate but no free lime.

Dicalcium Ferrite.—In the preparation of dicalcium ferrite, the sticks, composed of the proper proportion of ferric oxide and calcium carbonate, were heated to and held at a temperature of 1350°–1400° for three hours. In this preparation it was necessary to keep below 1436° as the compound dissociates at that temperature.[12]

Each of these compounds was ground to such fineness that 100 per cent passed through a 200 sieve.

The Rate of Hydrolysis

A. Hydrolysis when the Soluble Products are not removed.—The first experiment involved a determination of the rate of hydrolysis at 30° of the several constituent compounds when these were placed in a quantity of water

[9] Day and Shepherd: J. Am. Chem. Soc., 28, 1089 (1906).
[10] Bureau of Standards Technical Paper No. 78 (1917).
[11] First applied by W. C. Hansen in this laboratory.
[12] Sosman and Merwin: J. Wash. Acad. Sci., 6, 15 (1916).

sufficiently large that all of the $Ca(OH)_2$ contained in them would, if liberated, still fail to saturate the solution. The OH ion concentrations resulting in each case were determined at definite time intervals until no further change in pH with time was observed. These determinations served, therefore, both as a measure of the rate of hydrolysis, and as a measure of the total hydrolysis which had taken place.

In these experiments, 200 cc. of water, free from carbon dioxide, were used, and such a quantity of each compound as would result in the formation of 0.29 gr. $Ca(OH)_2$ if the lime which each contained were converted entirely into the hydroxide. Pure $Ca(OH)_2$ was used in the same amount in 200 cc. water as a standard of comparison. The reactions were carried out in tightly stoppered flasks to prevent contamination with the carbon dioxide of the air. The flasks were shaken from time to time to prevent the compounds from setting.

The OH ion concentrations of the resulting solutions were determined by the electrometric method with a saturated calomel half-cell, platinum-platinum black electrodes, and a Type K potentiometer. Results, reported in terms of pH, are given in Table II and plotted graphically in Fig. 1.

TABLE II

Hydrolysis of the compounds when the soluble products are not removed

Time in hours	OH ion concentration of resulting solutions expressed as pH						
	$Ca(OH)_2$	$3CaO.SiO_2$	$\beta 2CaO.SiO_2$	$\gamma 2CaO.SiO_2$	$3CaO.Al_2O_3$	$5CaO.3Al_2O_3$	$2CaO.Fe_2O_3$
1	12.10	11.56	11.08	10.91	11.70	11.43	10.25
3	12.28	11.62	11.16	10.98	11.89	11.44	10.42
24	12.29	11.86	11.33	11.07	11.92	11.46	10.82
96	12.29	11.95	11.42	11.19	11.93	11.46	11.00
192	12.28	12.01	11.45	11.24			11.10
288	12.28	12.00	11.47	11.27	11.93	11.45	11.12
384			11.47	11.28			11.12

From these results, it is evident that, under the conditions of this experiment, the amount of lime liberated by hydrolysis of tricalcium silicate and tricalcium aluminate is greater than that liberated by the other compounds, even though the total amount of lime present in the system is the same in each case. The calcium aluminates react with water very rapidly and reach an apparent equilibrium in about one day, while the calcium silicates and dicalcium ferrite require 8 to 12 days to reach this condition. The "lime liberated by hydrolysis" is not necessarily the total lime brought into solution, but only that part of the total lime as may be regarded as free calcium hydroxide. Lime in the form of calcium salts is not included by this term.

B. Hydrolysis when the Soluble Products are removed.—It has been found in the experiments just described that the compounds examined when placed in water, undergo hydrolysis, some of the lime being split off and going into solution as calcium hydroxide. When the solution is allowed to remain in contact with the solids, as above, equilibrium is eventually established be-

tween the solid phase and the calcium hydroxide in solution. Further experiments were undertaken to determine the nature of the hydrolysis which would result on the removal of the calcium hydroxide as it was formed in the solution.

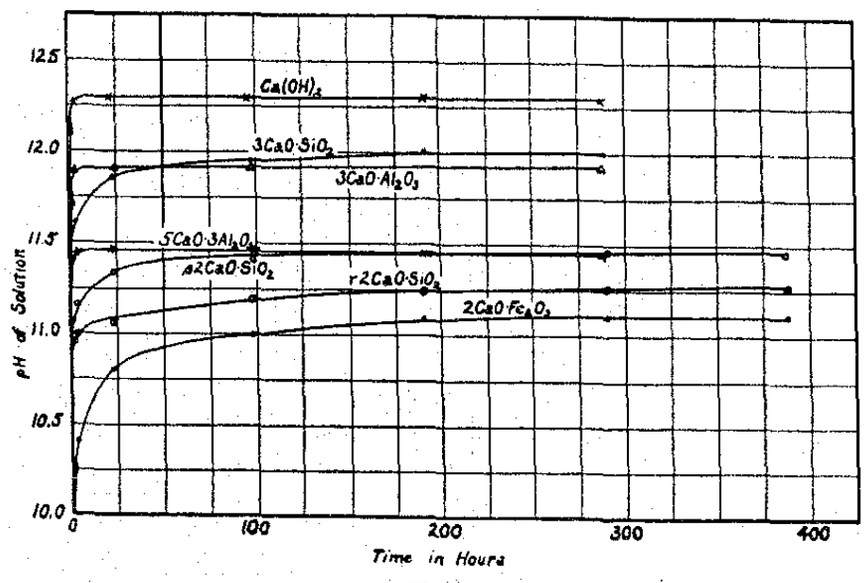


FIG. 1

Hydrolysis of cement compounds as measured by pH at varying time intervals, the total $Ca(OH)_2$ content in each case being 0.145 per cent.

Molar equivalent weights of the three silicates were used, (5 grams of $3CaO.SiO_2$, and 3.67 grams of $\beta 2CaO.SiO_2$ and of $\gamma 2CaO.SiO_2$). These amounts were employed because of the very rapid liberation of one mol of

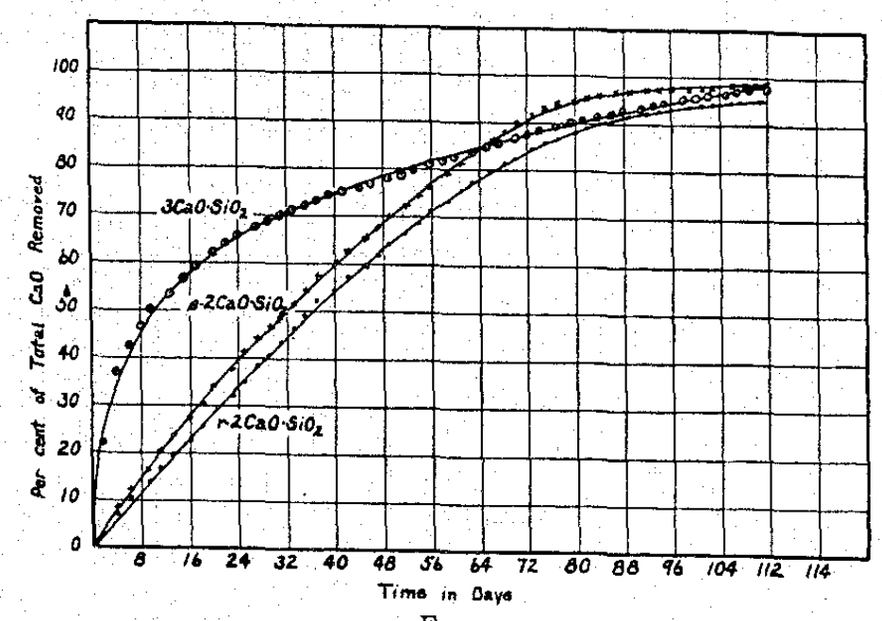


FIG. 2

Per cent of CaO removed from 3 CaO. SiO_2, β 2 CaO . SiO_2 and γ 2 CaO. SiO_2 at various time periods by intermittent extraction with water removed every 2 or 3 days.

CaO from the $3CaO.SiO_2$. The subsequent hydrolysis of the three residual silicates will then be somewhat more directly comparable as they will contain more nearly equal percentages of CaO. These were placed individually

in one liter quantities of distilled water and the flasks shaken several times a day to stir the contents and to prevent setting. Every second or third day 900 cc. of the supernatant solutions were siphoned off, and replaced by 900 cc. of distilled water. The amounts of lime removed in this manner were determined by titrating with standard hydrochloric acid aliquot portions of the solutions removed. The solutions contained a small amount of silica or silicates in each case.

Table II gives the amount and the percentages of the total lime removed from each compound at various periods of time up to 112 days, and Fig. 2 shows the percentages of the total CaO removed in solution plotted against the time.

The hydrolysis of tricalcium silicate proceeded so rapidly at first that in four days the amount of lime extracted was more than a third of the total lime present in the original compound. This is equivalent to about one mol. After this period, the extraction proceeded much more slowly. The rate of extraction of lime from beta dicalcium silicate slightly exceeded in this ex-

TABLE III

The Extraction of CaO from the Lime Silicates, at Room Temperatures

$3CaO.SiO_2$ Used 5 gr. 3.68 gr. CaO			$\beta 2CaO.SiO_2$ Used 3.67 gr. 2.39 gr. CaO			$\gamma 2CaO.SiO_2$* Used 3.67 gr. 2.39 gr. CaO	
Days	Grams CaO removed	% of total CaO removed	Days	Grams CaO removed	% of total CaO removed	Grams CaO removed	% of total CaO removed
2	0.8170	22.2	2	0.1197	5.0	0.1107	4.6
4	1.3620	37.0	4	0.2106	8.8	0.1863	7.8
6	1.5636	42.5	6	0.3015	12.6	0.2592	10.8
8	1.7139	46.5	9	0.3924	16.4	0.3312	13.8
10	1.8444	50.0	11	0.4833	20.2	0.4041	16.9
13	1.9695	53.5	13	0.5688	23.8	0.4752	19.9
15	2.0874	56.8	16	0.6543	27.4	0.5481	22.9
17	2.1882	59.5	18	0.7389	30.9	0.6201	25.9
20	2.2818	62.0	20	0.8199	34.2	0.6912	28.9
22	2.3529	64.0	23	0.9063	37.9	0.7659	32.0
24	2.4186	65.7	25	0.9828	41.1	0.8370	35.0
27	2.4807	67.4	27	1.0557	44.2	0.9081	38.0
29	2.5293	68.8	29	1.1259	47.0	0.9792	40.9
31	2.5797	70.0	31	1.1673	48.8	1.0040	43.7
33	2.6202	71.2	33	1.2366	51.6	1.1124	46.5
35	2.6508	72.0	35	1.3077	54.7	1.1844	49.5
37	2.6913	73.1	37	1.3680	57.2	1.2501	52.3
39	2.7300	74.2	40	1.4391	60.2	1.3122	54.8
41	2.7606	75.0	42	1.4922	62.5	1.3689	57.3
44	2.7983	76.0	45	1.5624	65.3	1.4283	59.7

* Days same as $\beta_2 Cas.SiO_2$.

TABLE III (continued)

46	2.8343	76.9	47	1.6128	67.5	1.4823	62.0
49	2.8703	78.0	49	1.6740	70.0	1.5426	64.6
51	2.9063	78.8	52	1.7352	72.6	1.5984	66.9
53	2.9441	80.0	54	1.7856	74.8	1.6542	69.2
56	2.9828	81.1	56	1.8378	76.9	1.7073	71.4
58	3.0134	81.9	59	1.8981	79.3	1.7613	73.7
60	3.0503	82.9	61	1.9431	81.3	1.8117	75.8
63	3.0881	83.9	63	1.9962	83.5	1.8612	77.9
65	3.1223	84.9	66	2.0574	86.1	1.9044	79.7
67	3.1565	85.7	68	2.1078	88.1	1.9458	81.5
70	3.1925	86.7	70	2.1510	90.1	1.9818	82.9
72	3.2231	87.5	73	2.1987	91.9	2.0187	84.5
74	3.2537	88.3	75	2.2293	93.3	2.0493	85.7
77	3.2843	89.3	77	2.2500	94.1	2.0790	86.9
79	3.3149	90.1	80	2.2653	94.8	2.1078	88.2
81	3.3455	90.9	82	2.2806	95.4	2.1330	89.3
84	3.3716	91.6	84	2.2959	96.0	2.1537	90.2
86	3.3959	92.3	87	2.3049	96.4	2.1753	91.0
88	3.4184	92.9	89	2.3103	96.7	2.1888	91.5
91	3.4409	93.5	91	2.3157	96.9	2.2014	92.1
93	3.4643	94.2	94	2.3193	97.1	2.2131	92.7
95	3.4841	94.7	96	2.3247	97.3	2.2248	93.1
98	3.5066	95.3	98	2.3301	97.5	2.2465	94.0
100	3.5264	95.8	101	2.3337	97.7	2.2573	94.4
102	3.5426	96.3	103	2.3382	97.9	2.2636	94.7
105	3.5579	96.7	105	2.3427	98.0	2.2699	94.9
107	3.5732	97.1	108	2.3463	98.2	2.2798	95.3
109	3.5876	97.5	110	2.3493	98.4	2.2870	95.6
112	3.6011	97.9	112	2.3523	98.5	2.2930	95.9

periment that from the gamma form, but both of these were far below that for tricalcium silicate at the early periods.

After 112 days the titration curves indicated that from 95 to 98 per cent of lime had been extracted from the several calcium silicates. At this point the remaining residue was filtered off, ignited and analyzed. The results are given in Table IV.

TABLE IV

Compound	Total Residue	SiO_2	CaO
$3CaO.SiO_2$	0.6466 gr.	0.6202 gr.	0.0240 gr.
$\beta_2CaO.SiO_2$	0.5040	0.4955	0.0085
$\gamma_2CaO.SiO_2$	0.6010	0.5882	0.0154

Thus the remaining residue was found to be almost pure hydrous silica with only a small amount of lime. There were originally present about 1.3 grams of SiO_2; the difference between this value and the amount found in the residues is to be accounted for in part by loss through solution and in part by mechanical loss on removing the solutions.

A most interesting observation obtained by an inspection of the curves is that the rate of extraction of the dicalcium silicates is nearly a straight line function of the time for about two months, but that after about 30 days (See also Table III) this rate is greater than that of the tricalcium silicate. After months there is very little difference in the three curves.

It appears to be impracticable to measure the rate of extraction of the calcium aluminates and the dicalcium ferrite in the above manner because of the solubility of the alumina and the ferric oxide in the lime solution and because of the presence of colloidal suspensions. Some of the alumina and the ferric oxide would doubtless be in molecular combination with the lime in one or more of the several possible intermediate hydrolytic products, some would be ionized in the solution, and some perhaps would be uncombined. There seems to be no reliable manner, in this case, for determining the partition of the compounds among these several products. It certainly would not be permissible to assume the total CaO content of the solution to be free Ca $(OH)_2$ resulting from hydrolytic cleavage. For these reasons a method involving the determination of the total line in solution would not be a measure of the rate of hydrolysis.

The end products of the hydrolysis, however, have been determined in another manner. Small quantities of $5CaO.3Al_2O_3$, $3CaO.Al_2O_3$ and $2CaO.Fe_2O_3$ were placed separately in Soxhlet extraction thimbles. These were suspended in separate flasks of distilled water and the solutions replaced by fresh quantities of water at frequent intervals. At the end of five months all of the lime had been extracted from the 5–3 calcium aluminate, but it required eight months to complete the removal of all of the lime from the tricalcium aluminate. The residue remaining in the thimbles at the end of these periods consisted, in each case, only of hydrous alumina, $Al_2O_3.aq$. It required but three months to complete the hydrolysis of the dicalcium ferrite, whereby a residue was obtained consisting entirely of hydrous ferric oxide, $Fe_2O_3.aq$.

Hydroxyl Ion Concentration of Hydrolytic Equilibria

As stated in the preliminary discussion, one of the objects of this investigation has been the determination of the hydroxyl ion concentration at which each of the several compounds neither combines with water in the reactions of hydrolysis, nor combines with base in the formation of compounds of higher basicity. This OH ion concentration would be expected to be different for each compound.

The experimental method consisted in noting the change in pH resulting upon adding the compounds to solutions of calcium hydroxide and sodium hydroxide. These will be treated separately.

A. Equilibria in Solutions of Calcium Hydroxide.—The pH of equilibrium of the several compounds was determined by placing 4 grams of the compounds in 200 cc. of calcium hydroxide solutions of varying concentration from zero to saturated. The use of 200 cc. of solution gave an ample quantity for pH determinations, and 4 g. of the compounds would be sufficient to make a measurable change in hydroxyl ion concentration of the solution if the solution and the compound were not in equilibrium. The samples were placed in an air bath maintained at 30° by means of a Beaver regulator.[13] The pH determinations were made at the same temperature. It was not necessary in in each case that sufficient time be allowed to attain complete equilibrium, but only that time be allowed for a partial reaction to take place which would indicate the direction of equilibrium.

At the end of a week, pH measurements were made on the original solutions and the solutions in contact with the cement compounds. The results are given in Table V.

When the three calcium silicates were placed in unsaturated solutions of calcium hydroxide, an increased pH always resulted, indicating that these compounds hydrolyzed with the formation and ionization of calcium hydroxide. When these compounds were placed in saturated calcium hydroxide, there was still a slight increase in pH. It seems necessary to conclude that these silicates continue to hydrolyze even in a saturated solution of calcium hydroxide. This is further demonstrated by the formation of crystals of calcium hydroxide on the sides of the flask. In the case of tricalcium silicate these crystals appear within 24 hours, both when placed in distilled water and in saturated lime water. When the dicalcium silicates are placed in saturated calcium hydroxide, the crystals appear after about 10 weeks, and when these compounds are placed in distilled water, 4 grams in 200 cc., the crystals appear in about 3 months.

The formation of the calcium hydroxide crystals apparently is due to the continued hydrolysis of the calcium silicates, even in saturated lime water, with the resultant formation of $Ca(OH)_2$ which crystallizes from the saturated solution.

The increase in pH which is noted in these samples over and above that obtained in a saturated solution of precipitated $Ca(OH)_2$ at the same temperature is of interest. Since crystals of the latter are present in many cases, being deposited on the sides of the flask, there cannot exist a permanent supersaturation, but a temporary supersaturation may account for the difference noted. Control tests have demonstrated that there is no appreciable reaction of the calcium hydroxide on the glass (Pyrex) and that the high pH values are not due to such reaction.

It might be expected that an apparent increase in the OH' ion concentration could result through the effect of the calcium silicate on the activity concentration of the calcium hydroxide. The degree of the observed increase however seems to be greater than would be expected by the very small con-

[13] J. Ind. Eng. Chem., 15, 359 (1923).

TABLE V

Change in pH obtained on placing compounds in calcium hydroxide solutions

Original $Ca(OH)_2$ solution Concentration in grams per liter	pH	pH of solution after 4 grams of the compound had been allowed to react with the solution for one week at 30°C.					
		$3CaO.SiO_2$	$\beta 2CaO.SiO_2$	$\gamma 2CaO.SiO_2$	$3CaO.Al_2O_3$	$5CaO.3Al_2O_3$	$2CaO.Fe_2O_3$
1.152*	12.37	12.45**	12.40	12.39	12.33	11.91	12.36
0.568	12.18	12.45**	12.35	12.31	12.24	11.75	12.32
0.210	11.83	12.43**	12.35	12.19	12.23	11.73	12.11
0.119	11.59					11.64	
Distilled H_2O	6.72	12.44**	12.12	12.02	12.07	11.61	12.06

* Saturated.
** Crystals of calcium hydroxide had formed on the sides of the flask.

centrations of the salt in solution. A further indication in favor of the view of supersaturation was furnished by analysis. A portion of the solution was separated from the tricalcium silicate after seven days, evaporated to dryness and analyzed for lime and silica. It contained 0.0025 gram SiO_2 and 1.286 grams CaO per liter. A saturated solution of calcium hydroxide at the same temperature contains 1.16 grams CaO per liter.

The other products of hydrolysis of these calcium silicates have not yet been definitely determined. Le Chatelier[14] believed that the hydrolysis continues until a hydrated monocalcium silicate ($CaO.SiO_2.2\frac{1}{2}H_2O$) is formed, that this is the principal constituent of hardened cements. On the other hand, Newberry and Smith[15] found that one sample of tricalcium silicate, after shaking with water, gave a varying residue of 1.5 to 2 equivalents of CaO to 1 of SiO_2, and a fused sample gave a hydrated silicate of the composition $2CaO.SiO_2.7H_2O$. Rankin [16] suggested that gelatinous hydrated silica might be released when the finely powdered tricalcium silicate is mixed with water, and that it is this silica which serves as the binding agent in concrete.

In studying the hydration of beta dicalcium silicate, Bates and Klein[10] found that this compound undergoes hydrolysis, resulting in the formation of crystals of calcium hydroxide large enough to be visible to the naked eye at the end of six months. We have also found this to be true of both the beta and gamma dicalcium silicate. Thus it seems that under these conditions a hydrated dicalcium silicate cannot be the final product of hydrolysis of the calcium silicates.

In our studies of the hydrolysis of the calcium silicates it was found that when the soluble products are not removed no one of the calcium silicates will give up all of the lime in combination. In each case an equilibrium was established between the calcium hydroxide in solution and some less basic calcium silicate.

On the other hand, a sample of freshly precipitated hydrous silica which had been placed in saturated calcium hydroxide solution for twelve months was found to have been changed, so that 97 per cent of the SiO_2 was acid soluble. The soluble residue had a composition 1.07 CaO:1SiO_2. This is evidence that a calcium silicate is formed by the interaction of calcium hydroxide in solution upon hydrous silica. It would not be expected, therefore, that the hydrolysis of a calcium silicate would proceed to the formation of any large amount of hydrous silica under conditions where an excess of calcium hydroxide is present.

The 5–3 calcium aluminate was found to undergo hydrolysis in all solutions of pH 11.6 or less but in solutions of pH 11.8 or more this aluminate enters into a reaction with the solution which causes the pH to decrease. This results from the combination of lime with the 5–3 calcium aluminate.

This reaction also has been demonstrated in another manner. A quantity of the 5–3 calcium aluminate was placed in a flask and covered with a sat-

[14] Bull., **42**, 82 (1900).
[15] J. Soc. Chem. Ind., **22**, 94 (1903).
[16] Trans. Faraday Soc., **14**, 23 (1918–19).

urated solution of calcium hydroxide. A thimble containing $Ca(OH)_2$ was suspended in the solution, the flask carefully sealed and set aside for 10 months. The thimble with the remaining insoluble material was then removed and the residue in the flask filtered off and analysed. The analysis of this residue was as follows:

	Grams	Mols
Al_2O_3	.1371	1
CaO	.2177	2.90

These experiments show that the $5CaO.3Al_2O_3$ combines with $Ca(OH)_2$. The first experiment shows this to take place when the calcium hydroxide is present in such amounts that the solution is brought to a pH of 11.8 or higher. An equation may be written:

$$5CaO.3Al_2O_3 + 4Ca(OH)_2 + aq. \rightleftarrows 3(3CaO.Al_2O_3.aq).$$

From the molar ratio of 2.90 CaO to 1 Al_2O_3 obtained in the last experiment, it appears that the compound $3CaO.Al_2O_3.aq.$ constitutes the major product in the de-hydrolysis of the 5–3 aluminate, when this reaction is carried out in the presence of a saturated solution of calcium hydroxide. It should be emphasized however, that the nature of the hydrolysis precludes the probability of any one compound being formed as an end product, to the complete exclusion of other compounds of different basicity. This will be apparent upon a consideration of the reactions suggested for the silcates given earlier in the paper.

Tricalcium aluminate undergoes hydrolysis when placed in calcium hydroxide solutions of pH 12.2 or less, and the resulting solution has a higher pH. But in no instance did this hydrolysis proceed far enough to produce an OH ion concentration equivalent to that of a saturated solution of calcium hydroxide. On the other hand when this compound is placed in saturated calcium hydroxide solutions, the pH of the resulting solution is always lowered slightly.

Kühl and Thuring,[17] and Lafuma[18] who have observed a similar phenomenon, believed the change to be due to the formation of a tetracalcium aluminate, but Radeff[19] attributes the change to adsorption of calcium hydroxide by the tricalcium aluminate.

That there is no appreciable quantity of tetracalcium aluminate formed under these conditions has been shown by a different means. Four grams of tricalcium aluminate were placed in a flask containing a saturated solution of calcium hydroxide. A Soxhlet thimble containing 0.83 gr. of CaO was then suspended in the solution and the flask sealed. After 15 months the flask was opened and the thimble with the remaining lime removed. A portion of the material on the bottom of the flask was found on analysis to contain:

0.1260 gr. Al_2O_3
0.2093 gr. CaO

[17] Zement, **13**, 243 (1924).
[18] Le Ciment, **1925**, 175.
[19] Zement, **14**, 177 (1925).

This is equivalent to a composition $3CaO.Al_2O_3$ and gives no indication of a reaction of lime with hydrated $3CaO.Al_2O_3$ to form $4CaO.Al_2O_3.aq$.

The dicalcium ferrite is found to hydrolyze in all concentrations of calcium hydroxide, which are less than saturated, but appears to be unchanged in saturated $Ca(OH)_2$.

B. Equilibria in Solutions of Sodium Hydroxide.—The hydroxyl ion concentrations obtainable with calcium hydroxide are limited by the low solubility of lime. It seemed desirable to measure the equilibria of these compounds in more basic solutions, and accordingly sodium hydroxide was used. All samples were treated in the manner previously described for calcium hydroxide solutions. The results of this study are given in Table VI.

The calcium silicates were found to react much the same in sodium hydroxide solutions as in those of calcium hydroxide. They all were found to undergo hydrolysis in the less alkaline solutions, producing an increase in pH and, eventually, a formation of calcium hydroxide crystals on the sides of the flask. However, as the concentration of the sodium hydroxide solutions increased, the pH changes decreased. This would be expected on the basis of the hydrolytic equilibria, for as the OH ion concentration is increased, the hydrolytic reaction potential will be decreased, and, at some definite value, will reach zero. At a pH of 13.7 there appeared to be no hydrolysis whatsoever. This was further borne out in this experiment by the failure of crystals of $Ca(OH)_2$ to appear on the sides of the flask even after eight months.

The 5–3 calcium aluminate reacts as with calcium hydroxide solutions. At pH values below 11.6 hydrolysis takes place, but at pH 11.8 and above the pH of the sodium hydroxide solutions is decreased. This indicates that combination is being effected between the compound and the base resulting in the formation of a more basic aluminate. In this case, sodium appears to substitute for calcium.

TABLE VI

Change in pH of constituent compounds of cement in solutions of sodium hydroxide

pH original sodium hydroxide solution	pH of solution after 4 grams of cement compounds had been allowed to react with solution for one week						
	$3CaO.SiO_2$	$\beta 2CaO.SiO_2$	$\gamma 2CaO.SiO_2$	$3CaO.Al_2O_3$	$5CaO.3Al_2O_3$	$2CaOFe_2O_3$
13.72	13.72	13.74	13.71	13.72	13.55	13.72
12.94	13.03	13.01	13.00	12.95	12.52	13.01
12.58	12.67	12.63	12.64	12.59	12.33	12.65
12.20	12.61	12.28	12.25	12.37	12.03	12.40
11.93	12.58	12.15	12.07	12.20	11.79	
11.53					11.63	
10.19					11.07	

The tricalcium aluminate also reacts in a similar manner as with calcium hydroxide solutions at pH of 12.2 and below. In these ranges hydrolysis takes place.

At pH values higher than 12.6, however, no change is observed. This indicates that hydrolysis can occur only below pH 12.2 and that above this value there is no combination with sodium hydroxide to form a more basic aluminate.

The dicalcium ferrite seems to hydrolyze in sodium hydroxide solutions which are below pH 13.0 but above this no change is observed.

Discussion and Summary

The experiments which have been described have been concerned primarily with the reactions of hydrolysis under several conditions, but the reactions of hydration proceed at the same time and cannot well be separated completely from the former. In all of the experiments studied, the hydrolyses have been brought about in the presence of quantities of water or solution much greater than can be present in a properly tempered mortar or concrete. The reason for this lies in the difficulty or uncertainty of following the course of the hydrolytic reactions except by examination of the resultant solutions. The latter procedure offers, at least, the most obvious method for such a study. With the data herein obtained, however, it is hoped to proceed to a more direct examination of the limits reached in the hydrolytic cleavage occurring during the processes of setting and hardening in the cements of commercial mortars and concretes.

In the experiment on the rate of hydrolysis *when the soluble products were not removed*, and the water was present in excess of that required to dissolve all the CaO, several points are of interest.

1. All of the six compounds studied undergo hydrolysis and give up $Ca(OH)_2$ to the solution but none of them give up all of their CaO to the solution, regardless of the time period. A condition of equilibrium appears to be approached in the case of each compound, whereby the lime in solution becomes sufficient greatly to retard or even to prevent further hydrolysis.

2. The $3CaO.SiO_2$ and the $3CaO.Al_2O_3$ give up by hydrolysis more lime as calcium hydroxide to the solution than the other compounds, and of these two, the $3CaO.SiO_2$ gives the greater amount. Next in order are β $2CaO.SiO_2$, $5CaO.3Al_2O_3$, $\gamma 2CaO.SiO_2$ and lastly $2CaO.Fe_2O_3$.

3. The calcium aluminates reached a condition of apparent equilibrium in one day, tricalcium silicate in eight days, all of the others attained this condition by the twelfth day. A point of interest is that the dicalcium silicates required only a little more time to reach this condition than was required of the tricalcium silicate under the conditions of this experiment.

In the experiments on the rate of hydrolysis *when the soluble products are removed*, it is brought out that:

4. The $3CaO.SiO_2$ loses a much greater percentage of its total content of CaO in periods up to about eighteen days than do the dicalcium silicates. The loss in the former case is very rapid at first, and becomes slight at later periods, while with both of the dicalcium silicates the loss is almost a straight line function of the time for about two months. Thus after eighteen days the rate of loss of CaO from these latter exceeds that from the $3CaO.SiO_2$. The

tricalcium silicate loses one mol (one third of its CaO) in three to four days, and 2 mols in twenty-four to twenty-six days. The beta dicalcium silicate loses one mol (one half of its CaO) in thirty-two days and the gamma form in thirty-six days. It may be pointed out that here again the dicalcium silicates show a lower rate of hydrolysis than the tricalcium silicate only in the early periods.

5. The end product of the above reactions (the soluble products being intermittently removed) appears to be hydrous silica and not a silicate. Thus at the end of about a month all of the silcates have been reduced to the composition $CaO.SiO_2.aq.$ but the hydrolysis proceeds continuously beyond this point.

6. The rate of hydrolysis of the aluminates and the ferrite could not advantageously be studied by this method, but the end products by dialysis, with the dialysate intermittently removed, have been found to consist of hydrous alumina in the case of the two aluminates and hydrous ferric oxide in the case of the dicalcium ferrite.

7. The time periods required to effect complete hydrolysis under the conditions of this experiment were approximately:

$5CaO.3Al_2O_3$,	5 months
$3CaO.Al_2O_3$,	8 months
$2CaO.Fe_2O_3$,	3 months

The experiments on the hydroxyl ion concentration of hydrolytic equilibria in solutions of calcium hydroxide and of sodium hydroxide showed several points of interest.

8. None of the three calcium silicates are in a condition of initial equilibrium in solutions of calcium hydroxide of any concentration. This is indicated not only by the increase in H ion concentration of calcium hydroxide solutions upon the addition of these silicates, but also by the continued deposition of crystals of calcium hydroxide in their solutions.

In solutions of sodium hydroxide the calcium silicates reached a pH of hydrolytic equilibrium at 13.7, which value was further confirmed by the failure of the silicates in such a solution to deposit crystals of $Ca(OH)_2$.

9. The end products in the hydrolysis of the silicates when the products are not removed, but in the presence of an excess of water probably consist essentially of $CaO.SiO_2.aq.$ and $Ca(OH)_2$. This conclusion is arrived at by deduction rather than by direct experiment. Thus both $3CaO.SiO_2$ and $2CaO.SiO_2$ (both forms) deposit crystals of $Ca(OH)_2$ from solution, showing that they hydrolyze, even in saturated lime water, to a composition of lower basicity than $2CaO.SiO_2$. However, hydrous silica is found to combine with $Ca(OH)_2$ when these are brought together. Hence some intermediate product between $2CaO.SiO_2$ and $SiO_2.aq.$ must be the most stable compound of silica in the presence of saturated $Ca(OH)_2$ and an excess of water. It seems probable that this most stable compound is $CaO.SiO_2.aq.$, but it will be recalled from the preliminary discussion that no one product can be expected to result

at equilibrium to the complete exclusion of all other hydrolytic products. Hence there probably results in saturated $Ca(OH)_2$ solution an equilibrium of silicate hydrates of low basicity.

10. The pH of hydrolytic equilibrium of $5CaO.3Al_2O_3$ is about 11.7 as determined both in calcium hydroxide and in sodium hydroxide solutions. The $5CaO.3Al_2O_3$ hydrolyzes in $Ca(OH)_2$ solutions only when the pH is 11.6 or less. At alkalinities of pH 11.8 and higher this aluminate combines with some of the CaO to form a more basic aluminate. Additional evidence obtained by allowing $5CaO.3Al_2O_3$ to remain in a solution of $Ca(OH)_2$ containing an excess of the base, indicates that the major product of the reaction of this aluminate in saturated $Ca(OH)_2$ solution is $3CaO.Al_2O_3.aq$.

11. The pH of hydrolytic equilibrium for the $3CaO.Al_2O_3$ is about 12.3 as determined both in calcium hydroxide and in sodium hydroxide solutions. At OH ion concentrations of pH 12.2 or less hydrolysis takes place. At OH ion concentrations of saturated $Ca(OH)_2$ solution, about pH 12.4, the introduction of the $3CaO.Al_2O_3$ lowers this value slightly. This may be due to the formation of a more basic aluminate ($4CaO.Al_2O_3$) or perhaps could be explained on the basis of a decreased solubility of $Ca(OH)_2$ in the presence of the tribasic aluminate.

12. The $2CaO.Fe_2O_3$ hydrolyzes in all solutions of $Ca(OH)_2$ that are less than saturated. In saturated solutions there is no change in pH but this does not determine the position of the equilibrium. In solutions of sodium hydroxide, the pH of hydrolytic equilibrium is found to be about 13.0.

Conclusions

The hydrolyses of several compounds which may occur in portland cement clinker have been investigated under various conditions. These compounds include $3CaO.SiO_2$, $\beta 2CaO.SiO_2$, $\gamma 2CaO.SiO_2$, $5CaO.3Al_2O_3$, $3CaO.Al_2O_3$ and $2CaO.Fe_2O_3$. The conditions under which these were investigated were made arbitrarily ideal in this preliminary study in order that the fundamental reactions of hydrolysis might be examined with the least possible interference due to uncontrolled physical factors or foreign salts. It is believed that:

1. the direction and relative rate of these reactions have been established in each case,

2. the OH ion concentrations required to prevent hydrolysis have been ascertained,

3. the nature of the probable end products has been determined throughout the possible range of concentrations.

All of the above experiments have been performed on pure materials and no attempt has been made in this study to learn the effect on the reactions due to the presence of more than one compound or to foreign materials. No attempt can be made at this time to correlate these data with the conditions met in cement mortars and concretes.

The essential conclusions may be set down as follows:

1. Each of the compounds studied was found to undergo hydrolysis as determined by the liberation of hydroxyl ions in aqueous solutions.

2. The relative rate of hydrolysis under the conditions studied, as measured by the pH of the solutions, indicates that the aluminates come to equilibrium more rapidly than the silcates and the ferrite.

3. The OH ion concentration necessary to prevent hydrolysis is different for the several compounds, as follows:

	pH
$5CaO.3Al_2O_3$	11.7
$3CaO.Al_2O_3$	12.3
$2CaO.Fe_2O_3$	13.0
$3CaO.SiO_2$)	
$\beta 2CaO.SiO_2$)	13.7
$\gamma 2CaO.SiO_2$)	

The pH of saturated $Ca(OH)_2$ at 30° is 12.4. Hence the aluminates do not hydrolyze in such solutions, the ferrite hydrolyzes slightly, and the silicates hydrolyze to a greater extent.

4. If the soluble products are intermittently removed, the silcates will hydrolyze eventually to hydrous silica, the aluminates to hydrous alumina, and the ferrite to hydrous ferric oxide. In each case $Ca(OH)_2$ is the other product.

5. If the soluble products are not removed, hydrolysis will proceed to the formation of $Ca(OH)_2$ and a less basic silicate, aluminate or ferrite. The composition of the end products in this case will be determined by the OH ion concentration and the amount of available water. In the presence of a large amount of saturated lime water, the silicates seem to go largely to a composition which may be represented by $CaO.SiO_2$.aq., and the aluminates to a composition $3CaO.Al_2O_3$.aq.

Bureau of Standards,
January 21, 1927.

THE CORRECTION OF CONDUCTIVITY DATA FOR THE CONDUCTIVITY OF THE SOLVENT

BY W. F. K. WYNNE-JONES

Although several authors have discussed the solvent correction and have suggested methods of applying it for aqueous solutions, no treatment has yet been given for non-aqueous solutions and even for water the application to dilute solutions is uncertain. Since it is just on these two fields of dilute and non-aqueous solutions that attention is at present being focused, a careful consideration of the correction seems desirable. In passing it is interesting to note that the problem of a solvent correction is most acute for conductivity data and is almost absent from data obtained by the electromotive force, freezing-point, and solubility methods. This is due to the fact that, whereas the activities of ions in dilute solutions are almost identical, their mobilities vary considerably and in consequence the replacement of one ion by another may have a considerable influence on the conductivity of the solution. Sometimes, however, as when weak electrolytes are present, the solvent correction may become important even for activity data.

Experimentally the criterion of a true solvent correction is that data obtained with different samples of solvent should agree with one another when corrected; while, to satisfy theoretical requirements, the correction must be attributable to some impurity whose effect can be calculated. When the theoretical check agrees with the empirical correction we are justified in considering the correction valid. For example, the conductivity of KCl in water at 18° C. has been determined by Kohlrausch and Maltby[1], and also by Weiland.[2] But whereas Kohlrausch and Maltby employed water of specific conductivity 1.0×10^{-6} reciprocal ohm, Weiland used water of conductivity 0.07×10^{-6} reciprocal ohms, yet, if in each case the conductivity of the water is subtracted from the data, the interpolated values for the equivalent conductivity of KCl at N/10000 become 129.0 and 129.04 and the agreement between these two figures leads us to believe that the correction has been properly applied; a conclusion which is borne out by the theoretical consideration that there will be no interaction between such a very dilute salt solution and any impurity which is likely to be present in the water and hence the water will retain its original conductivity even in the presence of the potassium chloride.

This method of applying the correction is valid whenever there is no interaction between the solute and the solvent, but if such an action occurs its employment is invalid and the chemical aspect of the problem must be taken into consideration. No one would treat a solution of sodium hydroxide as though it were a solution of sodium, yet it is almost as absurd to consider it

[1] Wiss. Abh. Phys. Tech. Reichsanstalt, 3, 156 (1900).
[2] J. Am. Chem. Soc., 40, 131 (1918).

simply as sodium hydroxide, for the two-fold reason that the hydroxyl ion will repress the ionisation of the water and that the sodium hydroxide will re-act with any impurity, such as carbon di-oxide, which is likely to be present. The neglect of this and similar considerations has led to may erroneous applications of the solvent correction, particularly in the field of non-aqueous solutions.

If these chemical reactions are taken into account, it is possible from a study of the conductivities of acids and bases in any solvent to deduce the nature of the impurity present in that solvent. Table I has been constructed in order to indicate the appropriate corrections when various impurities are present.

TABLE I

The Effect of Impurities on the Solvent Correction applied to Different Types of Electrolyte

Nature of Solute.	Solvent Correction. Acidic Impurity	Basic Impurity	Saline Impurity S S	S W	W S	W W
Acid S	None	Positive large	Normal	Positive small	Positive large	Positive large
W	None	Negative $1/K_a$	Normal	Negative small	Negative small	Negative
Base S	Positive large	None	Normal	Positive large	Positive small	Positive large
W	Negative $\propto 1/K_b$	None	Normal	Negative small	Negative small	Negative
Salt S S	Normal	Normal	Normal	Normal	Normal	Normal
S W	Normal*	Positive	Normal	Normal*	Normal*	Normal*
W S	Positive	Normal*	Normal	Normal*	Normal*	Normal*
W W	Normal	Normal	Normal	Normal*	Normal*	Complicated depends upon K_a, K_b, k_a and k_b

S & W indicate Strong and Weak.

S S means the salt of as strong acid and a strong base.

S W the salt of a strong acid and a weak base, etc.

K_a & K_b refer to the dissociation constants of a weak acid and a weak base, when present as solute.

k_a & k_b refer to the dissociation constants of the impurities.

Normal indicates that the solvent conductivity is subtracted from the data. When an an asterisk (*) is attached it implies that owing to metathesis the correction should be somewhat less than normal.

Positive, Negative indicate respectively that a correction is to be added and subtracted.

The corrections have been calculated on the basis of chemical interaction neglecting interionic forces, but, since they are usually dependent upon the differences in mobility of the ions, the assumption is made that the hydrogen ion and the anion of the solvent both possess higher mobilities than those of the other ions present. The correction for salt solutions does not include any hydrolysis correction and the corrected value will be that of the hydrolysed salt.

This table may of course be used either to determine the solvent correction when the impurity is known, or knowing the solvent correction, for estimating the impurity present: but, since the table only gives the sign, and not the magnitude of the correction, it is not possible to employ it for determining the nature of the impurity unless the form of the 'true' conductivity curve is known. Here we may be guided by a very general principle—that the equivalent conductivity of an electrolyte in dilute solution rises continuously with the dilution. An example of the application of this criterion is afforded by the data of Kohlrausch[1] for the equivalent conductivity of aqueous solutions of sodium hydroxide; these values rise continuously to a dilution of 200 litres after which they fall off rapidly. On the principle here adopted this falling off in very dilute solution must be due to the presence of an impurity and, in order to obtain the true values, a positive correction must be applied to the data, whence we see from the table that the impurity present is either an acid or the salt of a weak base.

But while this rule enables us to determine the nature of the impurity it is of no help in finding its actual amount or in determining the magnitude of the solvent correction. In order to do this some quantitative relationship must be employed and we at once meet the difficulty that any such relationship is open to criticism on either theoretical or empirical grounds. It is however possible to meet this criticism by comparing data for different classes of substances such as weak and strong electrolytes; for, while there is no reason to doubt that the former obey the law of mass action (after the correction for the interionic forces), the evidence is that strong electrolytes obey the square root law of Kohlrausch at any rate in aqueous and alcoholic solutions.

We thus adopt as our 'standards of behaviour'

(i) For weak electrolytes $$K = \frac{C\Lambda^2}{\Lambda_0(\Lambda_0-\Lambda)}$$

(ii) For strong electrolytes $$\Lambda = \Lambda_0 - bc^{\frac{1}{2}}$$

If, using the same sample of solvent, we find that the correction necessary for one type of electrolyte is the same as that required for the other, or, expressed differently, if from the correction empirically applied to the data for a weak electrolyte we deduce the correction for a strong electrolyte and find agreement with its empirical correction, then there is some justification for assuming that this correction is valid.

[1] Wied. Ann., **26**, 197 (1885).

It is important to emphasize this independence of assumptions and checking of results, since there is considerable danger of arguing in a circle and making the final result support the original assumption and vice-versa.

Aquecus Solutions

Several authors have considered the application of the water correction but the most thorough treatment is that of Kendall[1] who showed in a series of papers that the main impurity in conductivity water is carbon dioxide. His conclusions have not been generally accepted on account of the maximum observed at high dilutions in the data for strong acids. Since the publication of his papers fresh work has been done on the conductivities of acids and bases and, as the results are of considerably greater accuracy than those previously available it is possible to examine the problem more closely.

Kraus and Parker[2] have determined the conductivity of iodic acid at dilutions as low as .00005 N using very pure water and cells of quartz, Pyrex and soda glass. From the curves given in their paper the values in Table II have been interpolated:

TABLE II

Type of Cell	Specific Conductivity of Water	Λ for HIO_3 at Concentrations of			
		0.00164 N	0.001 N	0.0002 N	0.0001 N
Quartz	0.1×10^{-6}	381.8	384.4	388.5	389.0
	0.5×10^{-6}	381.8	384.4	387.2	386.6
Pyrex	0.5×10^{-6}	381.3	—	—	—
Soda Glass	0.24×10^{-6}	380.8	382.7	381.1	379.5
	0.8×10^{-6}	380.8	382.3	377.2	—

It is evident from Table II that the nature of the cell is of greater importance than the conductivity of the water and indeed it seems probable that it is the acid itself rather than the water which dissolves alkali from the glass: this conclusion is substantiated by the observation of Kraus and Parker that the conductivity of a N/500 solution of HIO_3 in a soda-glass cell decreased by .04% in 30 minutes and that on shaking a further decrease of the same order occurred.

In the light of this recent work we are able to reconcile the conflicting views of Kendall and of Whetham and Paine[3] on the nature of the impurity present in conductivity water. Whetham and Paine, and Paine and Evans[4] worked with strong acids in very dilute solution and, although they did not ignore the possible solution of alkali from the glass, they concluded that the impurity was the salt of a weak acid and weak base. Kendall, on the other hand, studied weak electrolytes, and, owing to the very slight solvent action on glass of an acid such as acetic, he assumed that his results supported the hypothesis that CO_2 alone was present in conductivity water.

[1] J. Am. Chem. Soc., **38**, 1480, 2460 (1916); **39**, 7 (1917).
[2] J. Am. Chem. Soc., **44**, 2429 (1922).
[3] Proc. Roy. Soc., **81A**, 58 (1908).
[4] Proc. Camb. Phil. Soc., **18**, (1914).

The most recent and accurate data for a strong base in water are those of Raikes, Yorke and Ewart[1] on the conductivity of sodium hydroxide. Although this work was carried out with water of a high degree of purity ($<.09\times10^{-6}$ reciprocal ohms at 18°C) and in spite of the care taken in preparing pure sodium hydroxide and in precluding any atmospheric contamination there is a pronounced falling off in the equivalent conductivity at high dilutions. An examination of the curves published in the above paper shows that this falling off is very much more marked than the similar effect observed in acid solutions. For example in Run K in which water of specific conductivity $.084\times10^{-6}$ reciprocal ohm was used a value of 208.3 was obtained for the equivalent conductivity at a concentration of 0.000254 N: the 'true' value at this concentration as interpolated from their graph is 215.8, while the difference between the mobility of the hydroxyl ion and a typical inorganic anion at 18°C is roughly (174 − 54 =)120. Hence the percentage of hydroxyl ion removed is 6.3 and, owing to the nature of the calculation, this probably is a minimum value. Comparing with this the conductivity of HCl at 25°C in water of specific conductivity 0.8×10^{-6} reciprocal ohm we find that at a slightly lower concentration, .0002521 N, Kendall[2] obtains a value of 420.1 while the 'true' value interpolated from Parker's data is 424.8 and, since the difference between the mobility of the hydrogen ion and a typical cation at 25° C is approx. 283, the percentage of hydrogen ion removed is found to be 1.6. Thus at the same concentration the effect of impurity in the water is four times as great for NaOH as for HCl and that in spite of the fact that the water employed for the sodium hydroxide solution possessed one tenth of the conductivity of the water used for the hydrochloric acid run.

This comparison is sufficiently striking to show that the main impurity in water is acidic in nature. In order to test Kendall's hypothesis that it is to be identified with carbon dioxide, it is most convenient to calculate the conductivities of solutions of sodium hydroxide on this assumption and to compare these values with the actual data. The curves in Fig. 1 have been constructed in this way assuming the following data for aqueous solution at 18°C.

Λ (for NaOH) $= 217.0 - 75.7C^{\frac{1}{2}}$ — Raikes, Yorke and Ewart.
Λ (for $\frac{1}{2}Na_2CO_3$ $= 114.0 - 150\ C^{\frac{1}{2}}$ — Landolt-Börnstein.
Λ (for $NaHCO_3$) $= 83.5 - 70\ C^{\frac{1}{2}}$ — Kendall.
$Kw = 1\times10^{-14}$
$k_1 = 3.1\times10^{-7}$ 1st dissociation constant of CO_2—Kendall
$k_2 = 6.0\times10^{-11}$ 2nd " " " —Johnston.

Curve I represents the conductivity of NaOH in water containing 0.02×10^{-5} moles of carbon dioxide per liter and of specific conductivity 0.09×10^{-6} reciprocal ohm.

Curve II corresponds to a carbon dioxide concentration of 1.2×10^{-5} moles per litre and a specific conductivity of 0.62×10^{-6} reciprocal ohm.

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[1] J. Chem. Soc., **129**, 630 (1926).
[2] J. Am. Chem. Soc., **39**, 13 (1917).

The points shown on the diagram are taken from two of Raikes, Yorke and Ewart's runs, B and K, in which water of specific conductivity 0.6×10^{-6} and 0.084×10^{-6} reciprocal ohm respectively was used. Run B is in moderate agreement with the theoretical curve II but there is no such concordance between K and curve I and it seems that the explanation of the deviation must be sought in the presence of some impurity other than carbon dioxide. It is probable that this disturbing effect is the solution of silica from

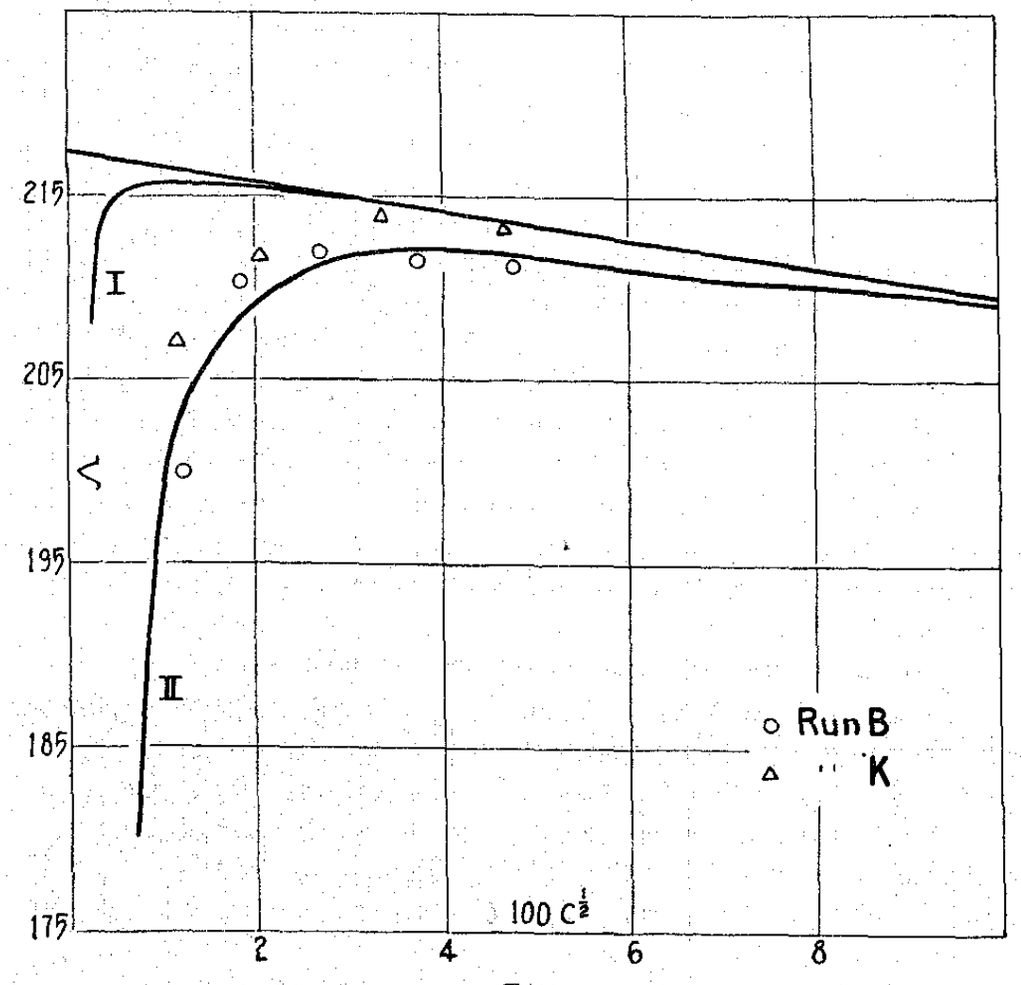


FIG. 1
The Conductivity of NaOH in water containing CO_2 at 18°C

the walls of the cell: when the carbon dioxide concentration is high, this would not be noticeable, but its influence becomes marked when very pure water is used.

Weak bases have not been examined in very dilute solution nor has any very recent work been published on the conductivities of their aqueous solutions. The classical work is that of Bredig[1], but this neither possesses sufficient accuracy nor extends to sufficiently dilute solution to enable any conclusions to be drawn from it. Kendall has stated that a positive correction should be applied to solutions of all bases but this is certainly erroneous. Weak bases usually require a negative correction, though, as with weak acids

[1] Z. physik. Chem., **13**, 289 (1894).

a strength is reached when no correction at all is required and then with still stronger bases the correction changes sign. This is due to the fact that neutralization of a weak base increases the number of ions but decreases the mobility due to the hydroxyl ion; the strength of the base determines which of these effects is predominant. This point is clearly brought out by the conductivity curve for the neutralization of a weak acid by a strong base.[1]

Summarising the results for aqueous solutions, we may say that in carefully purified water of conductivity less than $.8 \times 10^{-6}$ reciprocal ohm at 18°C the main impurity is CO_2 and that as a rule the water correction may be applied on this assumption. But when strongly acid and alkaline solutions are employed, the nature of the cell is of greater importance than the conductivity of the water and it is difficult to apply any exact correction.

Alcoholic Solutions

Although it is a matter of great interest and importance to apply the methods used for aqueous solutions to solutions in other solvents and to determine the solvent corrections for these also, it is very difficult to make such an investigation owing to the inadequacy of the data available. In fact the only solvents which have been studied sufficiently systematically are those most nearly allied to water itself and in particular the alcohols. Fortunately there are enough data in the literature for solutions in methyl and ethyl alcohols to enable at least a qualitative determination of the impurities present in these solvents, and in the remainder of this paper these data will be carefully discussed.

Before considering in detail the results for alcoholic solutions and drawing any conclusions regarding the nature of the impurities, it is necessary to discuss the methods of purifying these solvents and the possibility of introducing chance impurities during the purification. Probably water is the impurity, the removal of which is most desired and perhaps least completely effected. Many substances have been suggested for dehydrating alcohols and, with the exception of sodium, they are all efficient though with some the drying is a lengthy process. But what has been very largely overlooked is that even when the water content has been reduced to 0.01% the normality of the water still present in the alcohol is 0.005 N, and is actually greater than the concentration of the electrolyte in the region of very dilute solutions where the solvent correction is important. Hence it is not legitimate to treat the water as a small trace of impurity but rather as a constituent of a distinct solvent medium 99.99% alcohol, 0.01% water. In view of this it is evident that, so far as the solvent correction is concerned, the most noticeable impurities are those present in amounts smaller than the total concentration of electrolyte and it is very important to ensure that no method of drying the alcohol introduces any such impurity. As is pointed out later, dehydration by calcium is just such a method, since the nitride (which is always present in metallic calcium) reacts to form ammonia. This was first noted by Goldschmidt and

[1] Cf. Harned: J. Am. Chem. Soc., 39, 252 (1917).

Thuesen[1] who redistilled their alcohol from anhydrous sulphanilic acid in order to remove the ammonia: as mentioned by Hartley and Raikes[2] anhydrous copper sulphate seems to be equally efficient. The great effect of ammonia is shown by the data for hydrogen chloride in ethyl alcohol which are included in order to emphasize this point. Apart from these data, all the results given here have been obtained with alcohol purified according either to the method of Goldschmidt or to that of Hartley and where the conclusions established in this paper are found inapplicable it is probable that due regard has not been paid to the purification of the solvent.

Methyl Alcohol.

An examination of the data for this solvent shows that some of the complicating factors in the data for aqueous solutions are either absent or are of considerably less importance. Thus, for aqueous solutions of acids and bases, solution of the glass was found to be by no means negligible: in methyl alcohol this effect is not noticeable, which enables an unequivocal answer to be given to the question as to whether an acid or basic impurity is present in this solvent. But, as is shown later, the absence of this solvent effect is balanced by the effect of water although this concerns not so much the actual solvent correction as the quantitative explanation of the conductivity of the solvent.

Following the same argument as was adopted for aqueous solutions, we will first consider the data for strong acids. By far the most reliable data are those of Goldschmidt and Dahll[3] on the conductivity of hydrogen chloride at 25°C. The results of these authors extend to a dilution of 2560 litres and not only is there no maximum in the equivalent conductivity curve but the values, which are uncorrected for the solvent conductivity, are in quite good agreement with the square root rule of Kohlrausch which we have taken as our criterion of normal behaviour for a strong electrolyte. The present author has also carried out measurements of the conductivity of hydrogen chloride to a dilution of 10,000 litres and his results which will be published later also obey the square root rule. From this we are justified in saying that, if any impurity is present in the alcohol, it must be an acid whose ionisation is completely suppressed by the hydrogen chloride.

This conclusion is substantiated by the data for weak acids. Goldschmidt and Thuesen[4] have shown that the weak acids in methyl alcohol obey the Ostwald dilution law to a first approximation: it is noticeable, however, that their 'constants' all decrease with dilution—a variation of opposite sign to any which an impurity would produce, but the same as predicted on the basis of interionic forces.

While these results show fairly definitely that there is present in methyl alcohol a very weak acid, they do not enable us to determine either the concentration or the dissociation constant of this acid. In order to do this data for bases are required and the remainder of this section is devoted to a discusion of results obtained by the author for sodium methoxide and ammonia.

[1] Z. physik. Chem., **81**, 30 (1912).
[2] J. Chem. Soc., **127**, 526 (1925).
[3] Z. physik. Chem., **108**, 121 (1924).
[4] Z. physik. Chem., **81**, 30 (1912).

In Fig. 2 are plotted the results of three runs with sodium methoxide carried out by the methods described by Frazer and Hartley[1]: in run I alcohol of specific conductivity 1.00×10^{-6} reciprocal ohm was used, in run II the conductivity was 0.68×10^{-6} reciprocal ohm, and in run III, 0.11×10^{-6} reciprocal ohm. It is obvious that there is some impurity present which af-

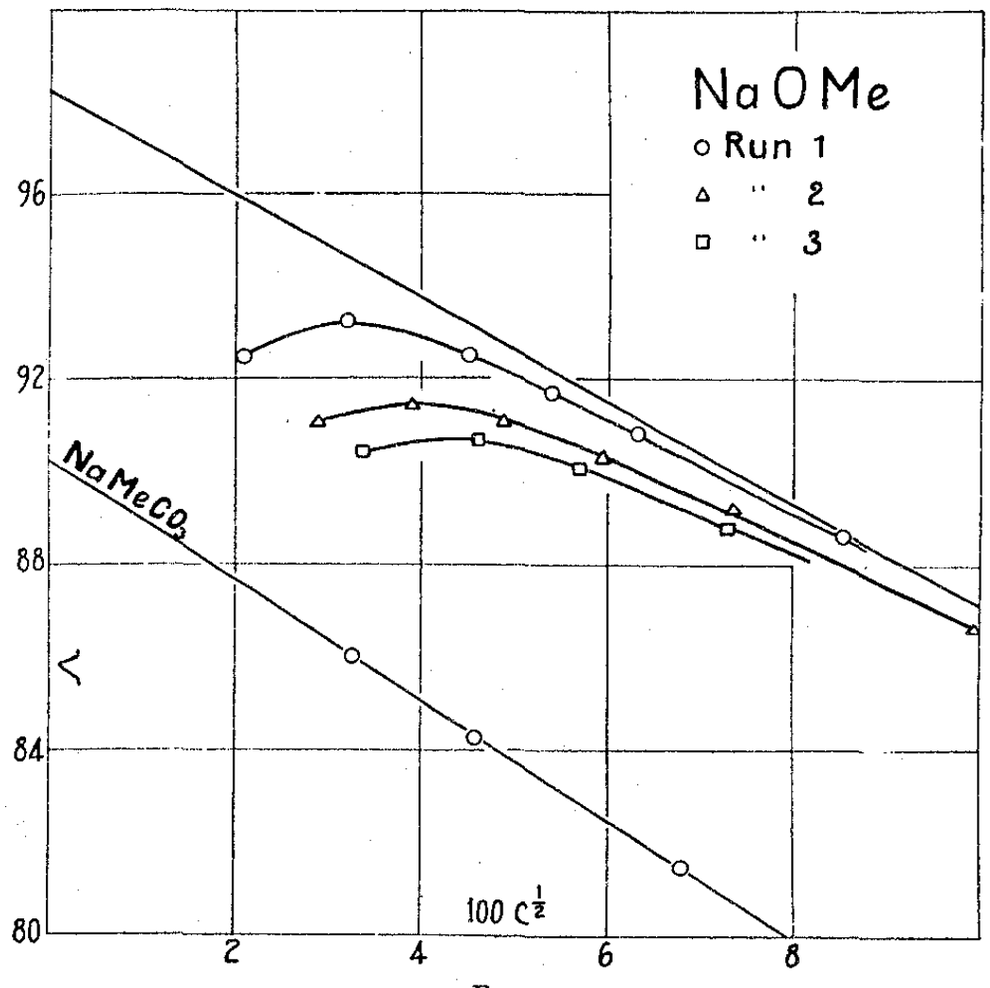


FIG. 2
The Conductivity of NaOMe in Methyl Alcohol at 25°C

fects both the conductivity of the alcohol and of the sodium methoxide. It seems possible to correct for this impurity on the basis of two assumptions:—

(1) That the square root rule is valid $\Lambda_o = \Lambda_c + bc^{\frac{1}{2}}$

(2) That the effect of the impurity is inversely proportional to the concentration of the solute. $\Lambda_c = \Lambda_{obs} + k/c$

The second assumption is tantamount to stating that the impurity is a monobasic acid and that there is no appreciable hydrolysis: it will undoubtedly cease to be true at very high dilutions when the concentration of the solute is comparable to that of the impurity. These two assumptions may be combined and expressed in the form

$$\Lambda_o = \Lambda_{obs} + k/c + bc^{\frac{1}{2}}$$

[1] Proc. Roy. Soc., **109A**, 351 (1925).

By solving equations of this type it was found that the results of different runs could be expressed by the equation

$$\Lambda_{obs} = 98.3 - 223c^{\frac{1}{2}} - k/c$$

where 'k' varies according to the conductivity of the solvent. The straight line in the figure above the sodium methoxide data is derived from this equation placing k = 0, i.e. when no impurity is present. Values interpolated from this curve are hereinafter referred to as 'true' values of the equivalent conductivity.

Since it was thought probable that carbon dioxide was the impurity present, the conductivity of the salt sodium methyl carbonate was determined and the results are shown in the figure as the lower straight line. The approach of the sodium methoxide curves to this line shews that the assumption is at least plausible, so, carrying the argument a stage further, we may calculate the amount of sodium methoxide which has been converted into the methyl carbonate. The observed conductivity of sodium methoxide will now be the sum of its true conductivity and the conductivity of the salt.

$$\Lambda_{obs} = (1 - X)\,\Lambda_{true} + X\Lambda_{NaMeCO_3}$$

Taking the most dilute point of run III we can substitue

$$93.48 = (1 - X) \times 93.01 + 87.6 \times X.$$

whence $X = 0.3$

and, as the total concentration is 1.089×10^{-4}N, the concentration of sodium methyl carbonate is 0.3×10^{-4}N, which must also be the concentration of carbon dioxide originally present in the alcohol. This value is based on the two assumptions already mentioned with the further assumption that the salt formed is sodium methyl carbonate.

In order to check this result an independent method of calculation is required and this is furnished by a consideration of the data for a weak base. Table III contains the data for ammonia which were obtained by the same method as were those for sodium methoxide.

TABLE III

The Conductivity of NH_3 at 25°C.

Normality	Λ	$K \times 10^6$
0.0003665	15.98	9.05
0.0006574	10.38	6.44
0.001242	6.56	4.70
0.001875	4.98	4.03
0.003270	3.47	3.36
*0.0310	0.809	1.69
*0.195	0.280	1.26
*0.4617	0.167	1.07

*These solutions were measured in a pipette cell.

These results are not corrected for the conductivity of the solvent which was 0.16×10^{-6} reciprocal ohm and it is apparent that some correction is required to bring the data into agreement with the dilution law but trial

showed that no fixed correction would effect this. If, however, we assume that the true dissociation constant of ammonia in methyl alcohol is 1.0×10^{-6} and that the increase with dilution is due to the formation of ammonium methyl carbonate we may write

$$\frac{[NH_4^{\cdot}] \times [OM\acute{e}]}{[NH_3]} = 1.0 \times 10^{-6}$$

and remembering that the observed equivalent conductivity gives a measure of $[NH_4]$ since the mobilities of the methoxide and methyl carbonate ions are not very different it is possible to calculate the approximate concentrations of all the ions present in the solution. The values given in Table IV have been arrived at in this way.

TABLE IV

Concentrations of the Ions present in Solutions of NH_3

Total Conc.	$[NH_3]$	$[NH_4^{\cdot}]$	$[OMe']$	$[MeCO_3']$
.0003665	.000304	.000062	.000006	.000056
.0006574	.000586	.000071	.000009	.000062
.001242	.001158	.000084	.000022	.000062
.001875	.001778	.000097	.000035	.000062
.003270	.003153	.000117	.000055	.000062
.0310	.03075	.000254	.000192	.000062

Apart from the most dilute solution, the concentration of the methyl carbonate ion is constant and leads to a value of 0.6×10^{-4} for the concentration of carbon dioxide originally present. The probable explanation of the slightly lower value obtained for the most dilute solution is that the alcoholysis of the salt is incompletely suppressed, if this is so the alcoholysis constant of ammonium methyl carbonate may be calculated

$$K_{alc} = \frac{[NH_3] \times [HMeCO_3]}{[NH_4^{\cdot}] \times [MeCO_3']}$$

$$= \frac{0.000304 \times 0.000006}{0.000062 \times 0.000058}$$

$$= 0.5.$$

This constant was also experimentally determined and the value obtained was 1.0. A consideration of the method of calculation shews that the agreement is as good as could be expected and corroborates the previous evidence that the impurity is carbon dioxide. From the alcoholysis constant the dissociation constant of carbon dioxide may be calculated by the equation

$$K_a = \frac{K_{me}}{K_b \times K_{alc}}$$

where K_{me} is the dissociation constant of methyl alcohol for which the present author has obtained a value of $2.0 \times 10-^{17}$. Adopting this value, we obtain

$$K_a = \frac{2.0 \times 10^{-17}}{1.0 \times 1.0 \times 10^{-6}}$$

$$= 2 \times 10^{-11}$$

as the dissociation constant of carbon dioxide.

In order completely to identify the impurity with carbon dioxide two further steps in the argument are required. Firstly, since for a weak electrolyte the specific conductivity is proportional to the square root of the concentration, the conductivity of the alcohol divided by the square root of the carbon dioxide concentration should be a constant. In order to test this the values obtained from the sodium methoxide data and from two separate ammonia runs are given

Solute	$\kappa \times 10^6$	$[CO_2] \times 10^4$	$\kappa \times 10^6 / [CO_2]^{\frac{1}{2}}$
NaOMe	0.11	0.3	2.0
NH_3	0.07	0.17	1.7
NH_3	0.16	0.6	2.0

This agreement is sufficiently close to show that the conductivity of the alcohol is probably due to carbon dioxide but the final proof would be the calculation of the specific conductivity of the alcohol, simply on the assumption that carbon dioxide is present. This may be done from a knowledge of its dissociation constant and its concentration in any particular sample of alcohol. Thus, taking the ammonia run in which the alcohol contained 0.6×10^{-4} equivalents of carbon dioxide per litre and assuming the approximate value of 190 for the equivalent conductivity of carbon dioxide at infinite dilution, the specific conductivity is calculated to be 0.01×10^{-6} reciprocal ohm whereas the observed value was 0.16×10^{-6} reciprocal ohm.

The obvious explanation of this discrepancy is that some salt is present, since a concentration of 0.01×10^{-4} equivalents per litre would suffice to account for the conductivity of the alcohol. This explanation however must be rejected for two reasons:—firstly the agreement of the data for hydrogen chloride with the square root rule would be destroyed if any correction were applied for the conductivity of the solvent; and secondly the relationship between the conductivity of the alcohol and the concentration of carbon dioxide as shewn by the ammonia and sodium methoxide runs could no longer hold, since the specific conductivity of a salt is proportional to its concentration while that of a weak electrolyte is proportional to the square root of the concentration. It is true that if the salt were one of a weak base or a weak acid (but not of a weak base and weak acid) the second objection would no longer apply, since the degree of hydrolysis of such a salt is proportional to the square root of the concentration, but the first objection would be even stronger since, as shewn in Table I, the correction would be positive and if the acid were weak would also be of considerable magnitude.

Since this explanation is ruled out there seems to be only one possible cause of the discrepancy and that is the presence of moisture in the alcohol. Goldschmidt has shewn that water has a very large effect on the conductivities of acids in alcohol and from his data for hydrogen chloride in methyl alcohol we find that at infinite dilution the conductivity is lowered by 1% when .01% of water is present. It is impossible by ordinary methods to ensure absolute dryness of alcohol or to estimate the minute quantities of water remaining so that it is quite probable that even the driest alcohol hitherto obtained con-

tains .01% of water. As mentioned earlier, although this seems a very small amount when expressed as a percentage, it is actually a solution of water of concentration approximately 0.005 N which compared either with the concentration of carbon dioxide (0.00006 N) or with that of the most dilute solutions of hydrogen chloride is quite a high concentration. If, on the basis of Goldschmidt's experiments we assume that water behaves as a weak base and combines with hydrogen ion then the concentrations of the base, of the hydrogen ion and of the basic ion must be governed by the relationship

$$K'_b = \frac{[H_3O^\cdot]}{[H_2O] \times [H^\cdot]}$$

and the relatively high concentration of water reduces this to the form

$$K''_b = \frac{[H_3O^\cdot]}{[H^\cdot]}$$

which explains why there is no maximum in the equivalent conductivity curve of hydrogen chloride at high dilutions as would be expected if only a trace of basic impurity were present. An analysis of Goldschmidt's data lends some support to this conclusion, for, comparing his results for dry alcohol and alcohol containing 0.02% of moisture, we find that at N/2560 the difference is 2.0% and at N/160 the difference is still exactly 2.0% but at N/10, the highest concentration measured, the difference has dropped to 1.4%. This shows that the effect of moisture is merely to displace the curve parallel to the original curve and not to alter its form until the concentration of hydrogen chloride exceeds that of the water.

In order to account for the specific conductivity of the alcohol the following relation must hold

$$x = 0.16 \times 10^{-6} = c\Lambda \times 10^{-3}$$

whence

$$c\Lambda = 0.16 \times 10^{-3}$$

It is probable that the hydronium ion ($OH_3^\cdot$) has much the same mobility as other cations so that we may take 100 as being the approximate value of the equivalent conductivity of the salt formed and so the concentration of the salt is 0.016×10^{-4} equivalents per litre.

We now have all the requisite data for determining the alcoholysis of the salt

$$K_{alc} = \frac{[H_2O] \times [CO_2]}{[H_3OMeCO_3]^2} = \frac{0.005 \times 0.6 \times 10^{-4}}{(0.016 \times 10^{-4})^2}$$
$$= 5 \times 10^5$$

and from a knowledge of the dissociation constants of methyl alcohol and of carbon dioxide the basic constant of water may be deduced.

$$K_b = \frac{K_{me}}{K_a \times K_{alc}} = \frac{2 \times 10^{-17}}{2 \times 10^{-11} \times 5 \times 10^5}$$
$$= 2 \times 10^{-12}$$

This is the first determination of the basic constant of water and it enables us to compare water with other bases: as shewn below water is very much weaker than most weak bases and indeed may for most purposes be

considered a neutral substance. But, as Brönsted[1] in a very suggestive paper has recently pointed out, the acidic and basic properties of a substance such as water may often be of extreme importance.

Base	K in H_2O	K in MeOH
NH_3	2.3×10^{-5}	1×10^{-6}
$C_6H_5NH_2$	4.6×10^{-10}	2×10^{-11}
H_2O	—	1×10^{-12}

Further consideration of this question of the basicity of water is deferred to a later paper in which the relations of acids and bases in aqueous and alcoholic solutions will be considered. Here it is sufficient to note that the basic nature of water is able to account for the behaviour of the carbon dioxide present in methyl alcohol.

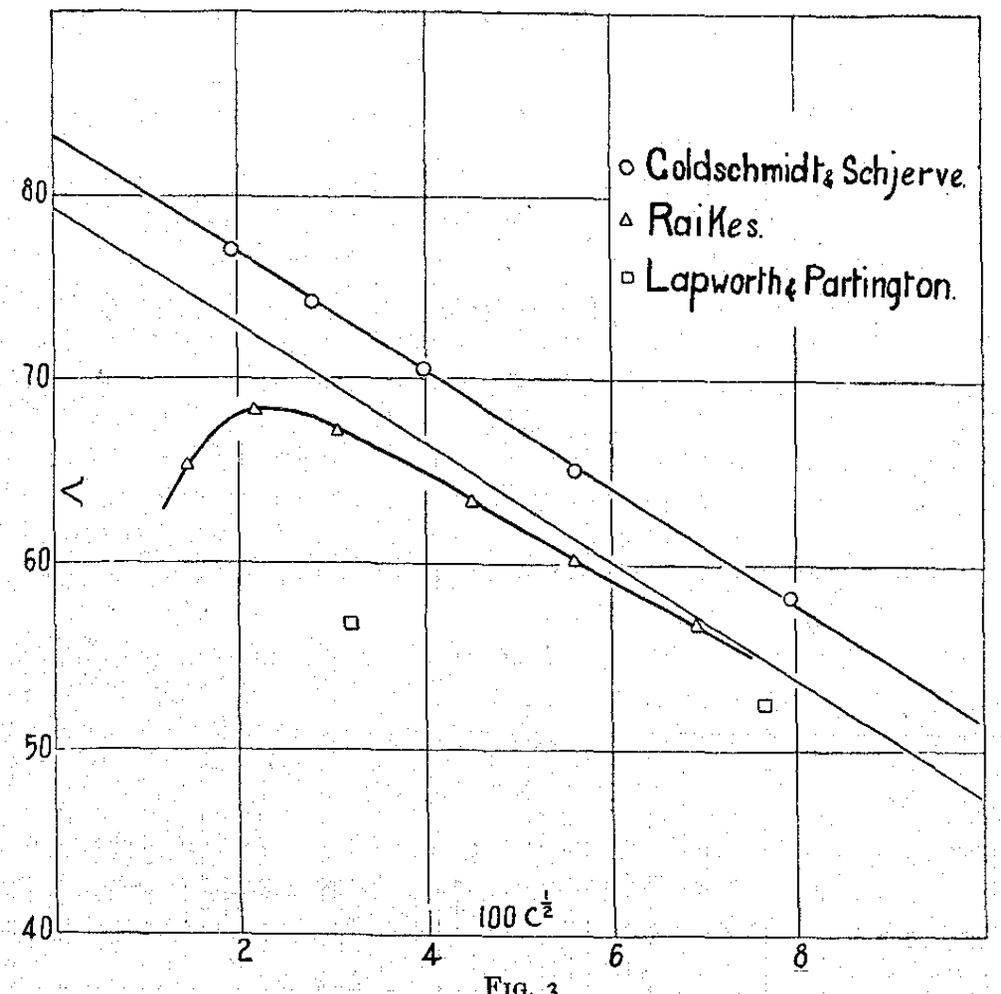


FIG. 3
The Effect of Ammonia on the Conductivity of HCl in Ethyl Alcohol at 25°C

Ethyl Alcohol.

The data of Goldschmidt for solutions of acids in this solvent show that their behaviour is almost the same as in methyl alcohol, so it is unnecessary to consider them in any detail. There is, however, a striking difference between his results and those of some other workers on the conductivity of hydrogen chloride, as brought out clearly in Fig. 3 where the results of Gold-

[1] J. Phys. Chem., 30, 777 (1926).

schmidt and Schjerve,[1] Lapworth and Partington[2] and some hitherto unpublished data obtained by Hartley and Raikes in this Laboratory are given. Partington's results alone are insufficient to indicate the cause of the discrepancy between his results and those of Schjerve but the form of Raikes'curves shows that there must be present a basic impurity which neutralises some of the acid. There is little doubt that this basic impurity is ammonia which as noticed by Goldschmidt is introduced by treatment with calcium—the method of drying employed by both Raikes and Partington. If Raikes' results are treated in the same way as the NaOMe data were in an earlier section the straight line below Schjerve's results is obtained: probably the difference between these two is due to moisture which has been shown by Goldschmidt to have a very large effect on the mobility of the hydrogen ion in alcohols.

The only available data for bases in ethyl alcohol are those of Robertson and Acree[3] on the conductivities of solutions of lithium, sodium and potassium ethoxides.

Their results are similar to those obtained for NaOMe in methyl alcohol but it is not possible to submit them to a closer analysis. The authors state that "correction has been made in all cases for the conductivity of the solvent" but, as each point was obtained by measurement of a separately prepared solution, and, as the individual values of the solvent conductivity are not given, it is impossible to attach an exact significance to the values at very high dilutions and any recorrection of the data would be meaningless.

For weak bases in absolute alcohol there are no data in the literature but the behaviour of strong bases makes it probable that these also will show in dilute solution divergencies from the dilution law similar to those observed for ammonia in methyl alcohol.

The data for ethyl alcohol are quite inadequate for any exact treatment of the solvent correction and it is only by analogy with methyl alcohol that we are justified in drawing any definite conclusion as to the impurity present, but the results of Goldschmidt and Schjerve together with the results of Robertson and Acree are in agreement with the hypothesis that carbon dioxide is present. In order to establish this definitely further work is required, more particularly on the conductivities of weak bases.

General Conclusions

It has been shown that a solvent correction may be applied to conductivity data in water, methyl and ethyl alcohols on the assumption that the impurity present in these solvents is carbon dioxide.

While it would be dangerous to generalize and assume that this statement is true for all solvents, yet it is evident that the complete removal of carbon dioxide is difficult, mainly owing to its presence as a normal constituent of the atmosphere, and in consequence it is probable that it will be present in

[1] Z. physik. Chem., **89**, 129 (1915).
[2] J. Chem. Soc., **99**, 1417 (1911).
[3] J. Phys. Chem., **19**, 381 (1915).

most solvents however highly purified. Its effect on conductivity data in any solvent will be determined largely by its solubility and the type of compound formed with the solvent.

When the impurity is known and its concentration and characteristics determined it is possible to apply the appropriate correction according to the methods described above. Even when these data are lacking a correction may still be applied when there is reason to believe that the dilution law or Kohlrausch's square root rule or some similar law is likely to be obeyed, but this method is only to be recommended as a last resource, or at best, as a check on one of the other methods.

In conclusion it must be emphasized that although a solvent correction can be made with some accuracy the ideal must always be its complete elimination. So far from its being desirable to employ a sample of solvent in equilibrium with the atmosphere, as recommended by Kendall, it is most necessary that a solvent employed for conductivity work should be prepared in the highest possible degree of purity in order to reduce this correction to the smallest possible dimensions. Only in this way can results be obtained free of all uncertainty.

I wish to thank Mr. H. Hartley, F. R. S., both for his very kind help and advice and also for permission to publish results obtained in this laboratory. I am indebted to the Department of Scientific and Industrial Research for the receipt of a maintenance grant during the progress of this work.

Physical Chemical Laboratory,
Balliol and Trinity Colleges,
Oxford.
May 2, 1927.

39A-101

THE EFFECT OF TEMPERATURE ON THE BASIC VISCOSITY OF ICE-CREAM MIXES

BY ALAN LEIGHTON AND OWEN E. WILLIAMS*

This paper shows that under normal temperature conditions the basic viscosity of ice cream mixes varies inversely with the temperature.

In a previous paper[1] it was shown that ice-cream mixes exhibit a true basic viscosity or, in other words, that when an ice-cream mix is stirred with sufficient vigor the viscosity drops to a certain value beyond which it is not lowered by continued stirring, at least under conditions encountered in the usual type of commercial ice-cream freezer. The change in value of this basic viscosity with variation in water concentration at constant temperature was shown to follow closely a slight modification of the empirical equation given by Arrhenius.[2] The modified form of the equation which is that of a straight line is

$$\log \eta = \Theta C + K \qquad \text{(Equation 1)}$$

in which equation, η is the viscosity in centipoises, C is the concentration in part solids to 100 parts water, and Θ and K are constants.

It was further pointed out that when C becomes zero, $\log \eta = K$, or the antilogarithm of K should equal the viscosity value of water at the temperature at which the measurements are made. The true viscosity value of water at 0° C. was only approximated in those experiments. The variation was attributed to errors arising from the fact that the concentration (C) was expressed in terms of parts solids in 100 parts water instead of in terms of molecular concentration.

When freshly prepared ice-cream mixes are allowed to stand at low temperatures they show a marked increase in viscosity. In commercial practice, freshly prepared mixes are usually held for a period of at least twenty-four hours before being frozen as it is the common belief that this increased viscosity is desirable. This procedure is known technically as ripening and is sometimes called aging.

Since this increased viscosity was found to be destroyed by mechanical stirring, it was pointed out that the increase must be due to the formation of a mechanical structure in the mix rather than to the hydration of the protein molecules, as it is difficult to see how hydrated water could be removed by mechanical force.

The above mentioned experiments were carried out at a temperature of 0° C. with three mixes of different basic concentrations. This paper gives the results obtained by determining the basic viscosity of different water concentrations of two mixes of essentially the same basic composition through a

[1] Alan Leighton and O. E. Williams: The Basic Viscosity of Ice Cream Mixes. J. Phys. Chem., 31, 596 (1927).

[2] Svante Arrhenius: Viscosity and Hydration of Colloid Solutions. Medd. Nobel Inst. 3 (13), 1–20 (1916).

temperature range of 8°C. to −1° C. The temperature range, which is near freezing, permits the temperature curve for each concentration to be extrapolated to the freezing temperature of that particular concentration. The viscosity value at the freezing temperature will then be the viscosity value of the unfrozen portion of the basic mix when this temperature is reached in the freezer. This point will be discussed later. The data of these two experiments are reported because they are more nearly complete than the data of a number of others carried out with mixes of different basic concentrations. However, the existence of the same viscosity relationships is shown in all cases.

As in the previous work, four concentrations of the basic mix were made up for this experiment. The highest concentration was prepared directly from cream, condensed skim milk, sugar, and gelatin. The basic viscosity of this mass was determined through the chosen temperature range. The mix was then diluted to the next concentration by the addition of cold water, the measurements repeated, and the work further repeated through the lower concentrations. Each complete series of temperature-concentration-viscosity measurements extended over periods of from three to four days.

For the determination of the basic viscosity, the laboratory, horizontal, brine-cooled, six-gallon ice-cream freezer was completely filled with the mix so that air could not be whipped in, and the dashers rotated at a speed of 175 R.P.M., the normal speed of the freezer. The temperature in the freezer was controlled manually. At frequent intervals samples were drawn from the freezer into small flasks, packed in shaved ice and carried to the viscometer which was immersed in a constant temperature bath adjusted to the temperature of the experiment. Two entirely separate batches of a normal ice-cream mix were used as the basis of the series of experiments here reported. Their basic composition was:

Fat	12.00
Sugar	14.00
Milk solids not fat	10.00
Gelatin	.30
	36.30
Water	63.70

Measurements of mix No. 1 were made at concentrations of 57.0, 70.0, 83.0, and 100.0 parts total solids to 100 parts water; and of mix No. 2 at concentrations of 56.99, 78.26, and 99.53 parts total solids to 100 parts water. In the latter series it was found impossible to get consistent measurements at concentrations of 120 parts total solids to 100 parts water. This was due, apparently, to the progressive precipitation of lactose from the mix. It should be pointed out here that the basic mix of normal concentration is practically saturated to lactose at a temperature of 0° C. This means that in nearly all of this work solutions supersaturated with lactose are being dealt with. Were it not for the unusual ability of lactose to form highly supersaturated solutions it would be practically impossible to get consistent results in these series of experiments.

Table I shows the viscosities for both series of experiments at four temperatures, also the calculated values of Θ and K. In Fig. 1 are given the straight-line curves obtained by plotting logarithmically against concentration the viscosity values at different temperatures for both series of experiments.

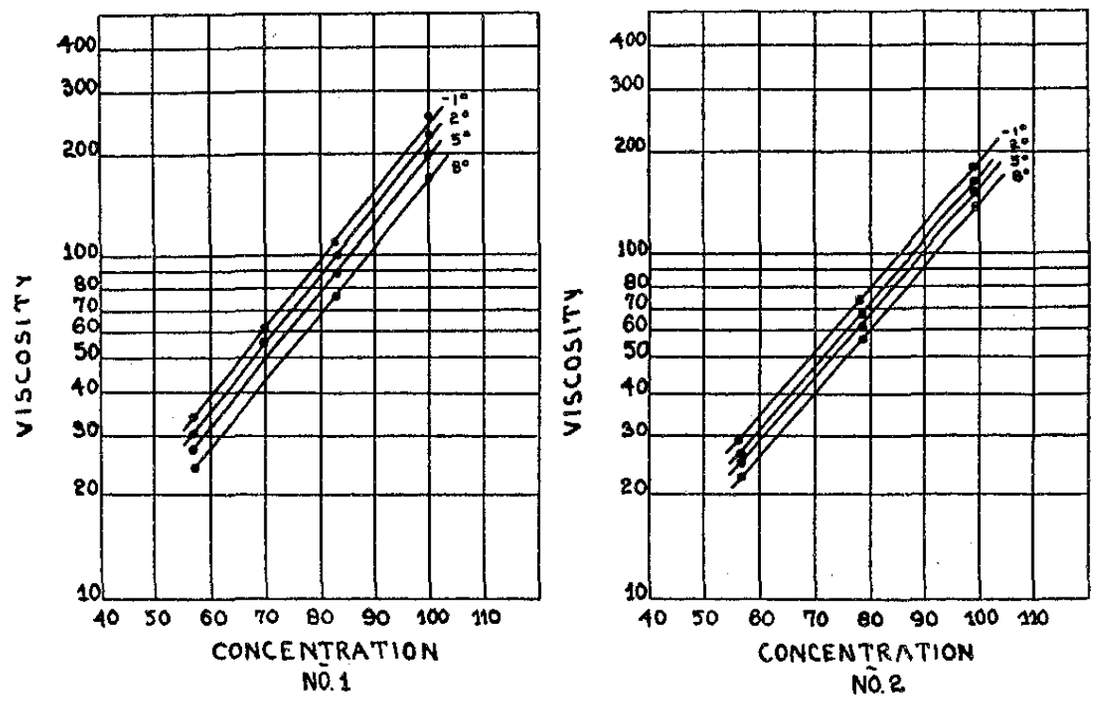


FIG. 1

The Relationship of Viscosity to Concentration at Different Temperatures of Mixes I and II

Although there is a slight variation in the value of Θ for the different series of measurements at the different temperatures, in each experiment this value can without any serious error be considered as a constant. The value of the constant K does, however, vary with the temperature. Since Θ gives the slope of the lines and is constant, it follows that the lines are parallel. The values of K determine the relative positions of the lines at the different temperatures. A direct plotting of the antilogarithms of K against temperature gives a straight line in both experiments, Fig. 2.

This means that within the temperature range of these experiments the viscosity value bears an inverse straight-line relationship to the temperature. A calculation of the value of K in terms of temperature gives the following relationships:

For experiment No. 1, $K = \log (2.3746 - .08233\ T)$

For experiment No. 2, $K = \log (2.5016 - .06355\ T)$

T is expressed in degrees Centigrade.

By substituting in equation 1, ($\log \eta = \Theta C + K$), the values of K determined empirically above, the following results are obtained:

For experiment No. 1, $\log \eta = .02006C + \log (2.3746 - .08237T)$ (Eq. 2)

For experiment No. 2, $\log \eta = .01860C + \log (2.5016 - .06355T)$ (Eq. 3)

TABLE I

The Viscosity—Temperature—Concentration Relationships of Ice Cream Mixes Nos. 1 and 2

1

Temp.	Concentration 57 Pts. Solids to 100 Pts. H_2O		Concentration 70 Pts. Solids to 100 Pts. H_2O		Concentration 83 Pts. Solids to 100 Pts. H_2O		Concentration 100 Pts. Solids to 100 Pts. H_2O		θ Av. 02006	K	Antilog K
	Visc in C. P.	Log V	Visc in C. P.	Log V	Visc in C. P.	Log V	Visc in C. P.	Log V			
8° C	24.61	1.3913	—	—	77.38	1.8886	170.0	2.2304	.01966	.2344	1.716
5° C	27.67	1.4420	—	—	87.92	1.9441	199.3	2.2995	.02005	.2914	1.956
2° C	30.72	1.4874	56.27	1.7503	98.43	1.9933	228.9	2.3595	.02006	.3453	2.215
−1° C	34.00	1.5315	60.49	1.7817	100.00	2.0385	257.9	2.4115	.02036	.3953	2.457

2

Temp.	Concentration 56.99 Pts. Solids to 100 Pts. H_2O		Concentration 78.26 Pts. Solids to 100 Pts. H_2O		Concentration 99.53 Pts. Solids to 100 Pts. H_2O		θ Av. 01860	K	Antilog K
	Visc in C. P.	Log V	Visc in C. P.	Log V	Visc in C. P.	Log V			
8° C	22.93	1.3604	56.46	1.7513	143.1	2.1525	.01848	.2994	1.993
5° C	25.32	1.4035	62.46	1.7956	157.5	2.1974	.01866	.3435	2.206
2° C	26.73	1.4270	67.79	1.8312	168.9	2.2274	.01854	.3723	2.360
−1° C	29.00	1.4624	74.56	1.8725	181.4	2.2588	.01873	.4092	2.565

These equations give the viscosity values of the two experimental mixes in terms of concentration and temperature.

As with any water solution ice separates from a liquid ice-cream mix when the temperature is lowered to the proper point. Further cooling causes a continued ice separation and a progressive concentration of the milk solids in the unfrozen portion of the mix.

The freezing-point-concentration relationships of the experimental mixes can also be calculated empirically.[1] Taking into consideration these data and

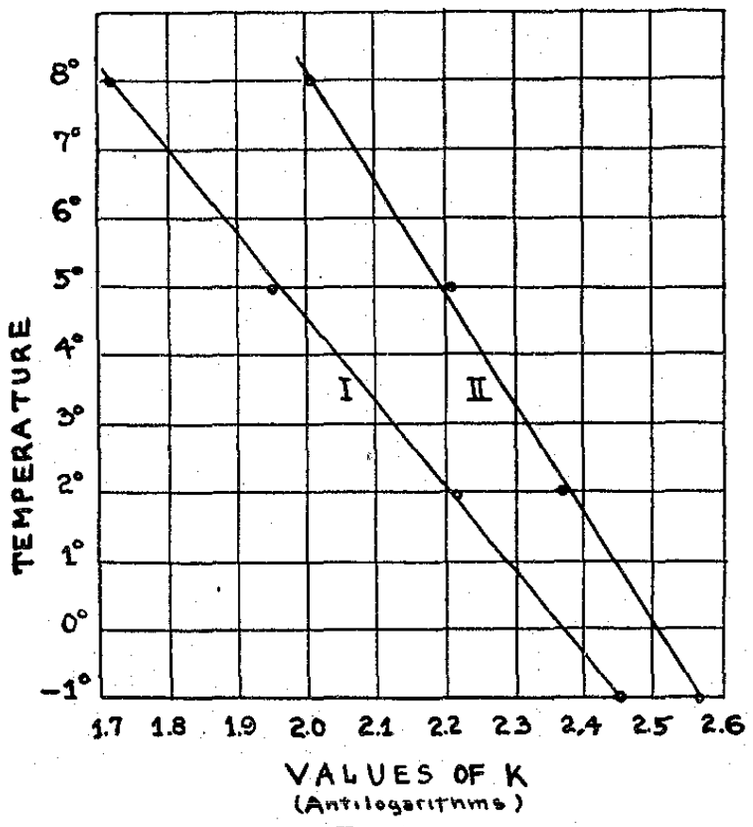


FIG. 2
The Variation with Temperature of the Antilogarithms of K

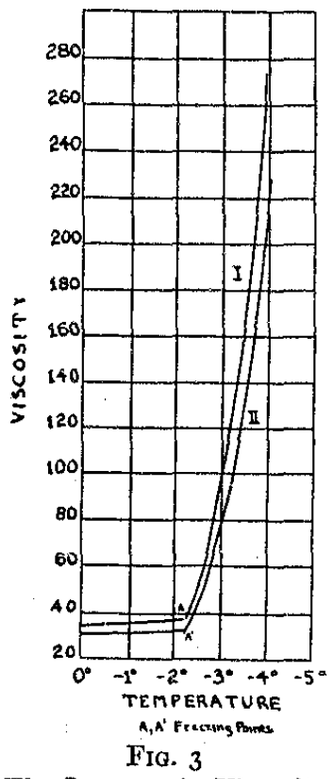


FIG. 3
The Increase in Viscosity of the Unfrozen Portions of Mixes I and II with Lowering Temperature during the Freezing Process

the measured viscosity-temperature-concentration relationships expressed in equations 2 and 3, and assuming that there is little or no supercooling, the change can be shown in the value of the viscosity of the unfrozen portions of the experimental mixes with the lowering of the temperature during the freezing process.

Since the experimental mixes Nos. 1 and 2 have identical basic composition they will have the same ice curve. Experiments have shown, however, that their viscosity values are different. Table II and Fig. 3 give the results of the calculations made to show the change of viscosity in the unfrozen portions of such mixes with change in temperature during the freezing process.

[1] Alan Leighton: On the Calculation of the Freezing Point of Ice Cream Mixes. J. Dairy Sci., 10, 300 (1927).

TABLE II

Freezing Points and Corresponding Viscosity Values of Four Concentrations of Nos. 1 and 2 Mixes

	CONCENTRATION				
	57 Pts. to 100 H^2O	57 Pts. to 100 H^2O	70 Pts. to 100 H^2O	83 Pts. to 100 H^2O	100 Pts. to 100 H^2O
Temp.	0°C	−2.25°F.P.	−276°F.P.	−3.28°F.P.	−3.96°F.P.
Visc. 1	33.02	35.60	65.98	122.3	273.9
Visc. 2	28.74	30.38	53.65	94.79	199.4

The great increase in the viscosity of the unfrozen portion of the mix in the ice-cream freezer during the freezing process is thus shown.

Conclusions: The experiments reported show that viscosity in ice-cream mixes bears an inverse linear relationship to temperature.

These relationships of temperature, concentration, and viscosity have been expressed by simple empirical equations.

The increase in the viscosity of the unfrozen portion of the ice-cream mix during the freezing process has been demonstrated. During the freezing process the lowering of the temperature results in an increase in the concentration of the milk solids and sugar in the liquid phase. This progressive concentration increase in the liquid phase increases its viscosity. The viscosity is simultaneously further increased by the effect of the temperature lowering itself. The combined effect of both temperature and concentration is shown.

THE INTERNAL ENERGY, MAXIMUM WORK, AND FREE ENERGY OF THE ELEMENTS

BY R. D. KLEEMAN

In a previous paper[1] the writer deduced directly from thermodynamics that the controllable internal energy of a substance or mixture under the pressure of its vapor is zero at the absolute zero of temperature. This particular internal energy only we deal with in thermodynamical processes. Its value of a substance at any given temperature and volume can evidently be calculated from specific heat measurements and other thermal data. The quantity is of considerable interest in itself apart from its important use in calculating the maximum work and the free energy. In this paper we will deal only with the elements whose heat capacity c_v at constant volume per gram atom is given by the equation

$$c_v = -\int\left(\frac{T}{\theta}\right) \qquad (1)$$

where T denotes the absolute temperature, θ is a constant depending on the nature of the substance, and $\int$ a function which is the same for all these substances, which are said to belong to Class I. The exact nature of the function $\int$ need not concern us here. The relation between c_v and T is best exhibited by a numerical table, such as Table I, which has been given by Lewis and Gibson.[2] If $\log\theta$ of an element of Class I is known its specific heat for a given temperature may then be found from this Table. The values of $\log\theta$ for the elements of this Class are given in Table II, and are also due to Lewis and Gibson.

The change in internal energy u on changing the temperature of a substance form the absolute zero to T at constant volume is given by

$$u = \int_0^T c_v.\partial T \qquad (2)$$

and represents the controllable internal energy of the substance in its final state. The value of u may most conveniently be obtained by plotting c_v against T on squared paper and counting the number of squares. In the case of a substance of Class I the values of T are obtained from the first and third column of Table I, having previously obtained the value of $\log\theta$ from Table II. The corresponding values of c_v are then obtained from the second and fourth column of Table I. In this manner the writer obtained the values of the internal energies in calories per gram atom for a number of the elements which are given in Table II, and refer to the absolute temperature 298°, and to the volumes they possess at the absolute zero of temperature. The Table also gives for comparison the entropies calculated by Lewis and Gibson. It will

[1] J. Phys. Chem., **31**, 747 (1927).
[2] J. Am. Chem. Soc., **39**, 2554 (1917).

be seen that the internal energies show a similar periodicity as the entropies, and may roughly be said to be numerically equal to about 100 times the entropy.

The maximum work A is given by

$$A = u - T S \tag{3}$$

It has been calculated for the elements in Table II, using Lewis and Gibson's values of the entropies, it will be seen that the values are numerically of the same order of magnitude as those of the internal energy.

The free energy F is given by

$$F = u - T S + pv = A + pv \tag{4}$$

where p denotes the pressure and v the volume of the substance in the final state. The pressure may be taken equal to one atmosphere, and v per gram atom is approximately given by

$$v = 2.6\sqrt{a_w} \tag{5}$$

according to Traube,[1] where a_w denotes the atomic weight relative to the hydrogen atom. Thus approximately

$$pv = \frac{2.6 \times 10^6}{4.19 \times 10^7}\sqrt{a_w} = .062\sqrt{a_w} \text{ cal.}$$

Hence pv is negligible in comparison with A, and the free energy is very approximately equal to the maximum work.

A complex substance may undergo a remarkable change at the absolute zero of temperature, as will now be shown, which has an important bearing on the calculation of the internal energy. Let us pass a number of substances through the following cycle:

a) Mix them isothermally in a reversible manner, which we will suppose gives rise to the formation of new molecules, and let ΔU denote the increase in internal energy.

b) Lower the mixture in temperature to the absolute zero of temperature under any given conditions. The increase in internal energy is $-\int_0^T c_i.\partial T$, where c_i denotes the internal specific heat.

c) Separate the constituents isothermally in a reversible manner and let $-\Delta u_{T=0}$ denote the increase in internal energy.

d) Increase the temperature of the constituents to T under conditions so that they are in their initial state, and let $\Sigma\int c_i.\partial T$ denote the increase in internal energy.

On equating the change in internal energy to zero we obtain

$$\Delta u - \Delta u_{T=0} = \Delta\int_0^T c_i.\partial T \tag{6}$$

Now Δu is usually so large that if we suppose $\Delta u_{T=0}$ small or equal to zero, its value cannot conceivably be represented by the integral term. The aver-

[1] Physik. Z., 1909, 667.

age value of c_i would have to be often of the order of a thousand calories per degree. It is highly improbable that the specific heat could ever possess such high values, at least they have not yet been observed. The value of $\Delta u_{T=0}$ must therefore under these conditions be finite and often quite large. Now we may write

$$H_m = \Delta u + A \tag{7}$$

where H_m denotes the heat absorbed on combining the substances at the temperature T, and which is given by

$$H_m = T\left(\frac{\partial A}{\partial T}\right)_v \tag{8}$$

where A denotes the external work done during the process. According to the latter equation $H_m = 0$ when $T = 0$, and hence

$$\Delta U_{T=0} = -A \tag{9}$$

Thus $\Delta u_{T=0}$ and A cannot be independently zero under these conditons. Now if the substances and the mixture exist under their vapor pressures at the absolute zero of temperature it can be shown that $A = 0$. For we may suppose that the substances are evaporated, the vapors mixed and then condensed. The external work done has the form ΔRT, which is zero since $T = 0$. Therefore in the case that $\Delta u_{T=0}$ is not zero, A is not zero, and one or more of the substances we are dealing with exert a great external pressure when the absolute zero is reached. If no counter pressure were exerted the substance would explode. It is on account of the necessity of exerting this counter pressure that A and hence $\Delta u_{T=0}$ is not zero. This pressure can be shown to be in most cases enormous, tending to explode the substance as if it were an explosive. It cannot be caused by molecular motion of translation since the temperature is zero. It is probably caused by a change in the electronic configuration of the atoms when the absolute zero is reached calling large forces of repulsion into play.

If a substance which suddenly exerts a high pressure when it reaches the absolute zero of temperature is allowed to expand isothermally till its pressure is zero, it arrives at its zero of controllable internal energy. During the expansion its internal energy decreases by an amount equal to the external work done. The entropy however undergoes no change since the adiabatic of zero entropy includes the various states at the absolute zero of temperature. Thus the data from which the entropy of a substance may be calculated is not in all cases sufficient for calculating the internal energy.

An example of this kind presented itself in calculating the internal energies of the elements. Lewis, Latimer, and Gibson,[1] give the revised values 1.688 and 1.800 of log θ for white and gray tin respectively. On calculating the internal energies as described we obtain for white and grey tin respectively the values 1362 and 1265 cal. The difference between the two values should be equal to the increase in internal energy on gray tin getting transformed into white at 19°C., which Brönsted[2] has determined to be equal to 541 cal.

[1] J. Am. Chem. Soc., **44**, 1008 (1922).

[2] *Z.* physik. Chem., **88**, 479 (1914).

But the difference is equal to only 97 cal. On the other hand Lewis, Gibson, and Latimer, obtained 578 for the value of $-T\Delta S$ from the same data, which agrees well with the value 557 of $\Delta F - \Delta H$ found from other thermal data. We have therefore here a case of the kind discussed. White tin in getting transformed into gray tin at the absolute zero of temperature is attended by a decrease in internal energy equal to 444 cal. This indicates that of the two forms the gray is stable under the pressure of its vapor at the absolute zero of temperature, and its controllable internal energy therefore zero under these conditions, while the white tin is unstable. The internal energy of gray tin at 298° K is therefore equal to 1265, the value obtained from specific heat measurements, and the value of white tin equal to 444 plus 1362 equalling 1806. The revised entropies given by Lewis, Gibson, and Latimer are 11.17 and 9.23 for white and gray tin respectively, by the help of which the maximum work can be calculated to be -1523 and -1486 cal. respectively. If an element exist in one form only we may be fairly certain that the internal energy calculated from specific heat data is correct.

White tin is known to be unstable at temperatures below 18°C., which is in line with the foregoing result. But a substance may be quite stable down to the absolute zero of temperature, it should be noted, and then suddenly become unstable with the evolution of a large external pressure. This pressure in the case of white tin, taking the change in density to be roughly from 6 to 7, has the average value of 3000 atmospheres.

It may happen that a substance becomes unstable and violently expands before the absolute zero of temperature is reached, say at the temperature T. If it is allowed to expand at this temperature under the high pressure it exerts the heat Q absorbed will be small in comparison with the heat of formation because the change in entropy Q/T cannot be large. The external work is done at the expense of the liberated internal energy which we have seen would be of the order of magnitude of the internal heat of formation ΔU. This liberation of energy is probably accompanied by marked chemical changes such as the decomposition of the substance, in fact we would expect that the inverse process takes place that gives rise to ΔU, so that after the expansion we are dealing with a mixture under low pressure whose constituents could be separated from each other without a great change in internal energy taking place. Since the change in internal energy during expansion is likely to be large this holds also for the pressure exerted which may accordingly be of the order of thousands of atmospheres. If the expansion of the substances were prevented by the application of a sufficiently high pressure, its specific heat would probably remain more or less normal down to the absolute zero of temperature.

It is usually possible to predict whether or no a given substance is likely to be stable under its vapor pressure at the absolute zero of temperature from considerations of the heat of combustion and other thermal data.

The internal energies of various complex substances will be calculated in a subsequent paper in which the investigations of this paper will find further application.

TABLE I

log T/θ	c_v	log T/θ	c_v
−0.6	0.11	+0.40	5.26
−0.5	0.21	+0.50	5.49
−0.4	0.43	+0.60	5.65
−0.3	0.84	+0.70	5.72
−0.2	1.43	+0.80	5.76
−0.1	2.19	+0.90	5.78
0.0	2.98	+1.00	5.79
+0.10	3.78	+1.10	5.80
+0.20	4.43	+1.20	5.81
+0.30	4.91		

TABLE II

	log θ	S_{v298}	U_{v298}	$-A_{v298}$
Lithium	1.928	7.41	1130	1078
Beryllium	1.945	7.18	1113	1026
Sodium	1.622	11.43	1466	1940
Magnesium	1.863	8.25	1200	1259
Aluminum	1.970	6.85	1056	985
Calcium	1.709	10.29	1303	1756
Titanium	1.994	6.57	1040	918
Chromium	2.063	5.70	949	750
Manganese	1.944	7.19	1111	1031
Iron	1.996	6.54	1037	912
Nickel	1.950	7.11	1100	1018
Cobalt	1.950	7.11	1100	1018
Copper	1.890	7.92	1170	1190
Zinc	1.754	9.66	1326	1552
Zirconium	1.773	9.41	1306	1498
Molybdenium	1.925	7.45	1226	994
Ruthenium	1.974	6.80	1123	903
Rhodium	1.921	7.49	1085	1147
Palladium	1.822	8.80	1307	1325
Silver	1.738	9.89	1329	1618
Cadmium	1.627	11.38	1410	1980
Lanthanum	1.459	13.60	1521	2531
Cerium	1.450	13.71	1527	2558
Tungsten	1.860	8.29	1208	1267
Osmium	1.901	7.78	1168	1150
Iridium	1.838	8.60	1247	1316
Platinum	1.737	9.91	1337	1616
Gold	1.669	10.81	1389	1832
Mercury	1.449	13.73	1516	2576
Thallium	1.421	14.10	1431	2771
Lead	1.390	14.52	1535	2791
Thorium	1.462	13.58	1507	2540
Uranium	1.650	11.07	1376	1915

SOCIÉTÉ DE CHIMIE INDUSTRIELLE
28, Rue St-Dominique
PARIS
ANNUL
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ADHESIVES AND ADHESION: GUMS, RESINS AND WAXES BETWEEN POLISHED METAL SURFACES*

BY JAMES W. McBAIN AND W. B. LEE

It is of interest to collate some of the definite regularities which are emerging from our investigations on the laws of adhesion.[1]

True adhesion to smooth, polished or crystalline surfaces, where the adhesion is necessarily specific, is the most interesting type. This is exhibited not only by the common recognised adhesives, but by pure crystalline chemical substances, and the magnitude of the effect may amount to one or more tons per square inch. Such joints often exceed by several fold the tensile strength of the adhesive itself. It is illuminating that there is an unmistakable although imperfect parallelism between the strength of such joints and the intrinsic properties of the materials joined and those even of the adhesive itself. Such properties include internal pressure, tensile strength, elasticity, hardness, and conversely compressibility and atomic volume. Probably these regularities extend to the adhesives themselves where these are homogeneous; but adhesives involving a solvent, such as glues and silicates, are not directly comparable with such others as shellac or tri-nitro-toluene.

The thinner the layer of adhesive the stronger the joint; the strength is increasing very rapidly when the adhesive layer is reduced to a millionth of an inch in thickness. It is evident that liquids are modified and immobilised in the immediate neighborhood of solid surfaces and that either the range of molecular attraction approaches the magnitude named, or that more probably not only are the molecules which actually touch a surface oriented, but that through a sort of chain effect (or in certain cases micellar linkage) this influence extends rather deeply into the body of the liquid or subsequently solidified liquid.[2] The effect of such orientation and the resulting disparity of properties with change of direction is illustrated by the antibatic relation between lubricants and adhesives and by the similarity between the strength of joints in tension and in shear. It appears that disorderly arrangement of molecules results in maximum strength, and that there is a close connection between adhesion and the architecture of the molecule.

*Investigation carried out in the Department of Physical Chemistry, University of Bristol for the Adhesives Research Committee of the Department of Scientific and Industrial Research, Great Britain. Published by permission of the Department of Scientific and Industrial Research. Our thanks are due to Principal Andrew Robertson for the facilities placed at our disposal in the Faculty of Engineering, University of Bristol.

[1] For previous papers see McBain and Hopkins: J. Phys. Chem., **29**, 188-204 (1925); **30**, 114-125 (1926); Second Report of the Adhesives Research Committee, Appendix IV, 34-89 (1926); McBain and Lee: Proc. Roy. Soc., **113A**, 606-620 (1927); J. Soc. Chem. Ind., (1927), Ind. Eng. Chem. Sept. (1927).

[2] In a separate communication by McBain and G. P. Davies (J. Am. Chem. Soc., **49**, Sept. (1927)) absolute measurements of adsorption in the air-water interface are adduced and this conception elaborated as a result. For example, it explains the rigidity of liquids in which inert particles are suspended as shown by the coefficient of viscosity varying with rate of shear, a phenomenon stressed by Hatschek, for which he has been at a loss to account.

7674

Other regularities which have been found are not so directly connected with the subject matter of the present paper because they relate to mechanical joints, to the great practical importance of mechanical properties other than tensile strength, and to the effect of humidity upon the tensile strengths of joints using aqueous adhesives such as glue.

The present paper adduces some preliminary measurements to show the way in which joint strength increases with thinness of adhesive layer over a wide range, especially when the film is the thinnest possible. In addition data are given with regard to the strength of joints between metals using such adhesives as waxes, shellacs, gums and resins which are of increasing importance owing to the development of the lacquer industry.

In nearly all cases the adhesive was employed in the molten state, the temperature of the metal test-pieces being only just above that of the molten adhesive. The test-pieces were generally of the same form as those used by McBain and Hopkins (l.c.); but, in a few experiments, test-pieces of larger area were prepared with a view of minimising the influence of experimental errors on the final results. In the experiments with optically polished surfaces, test-pieces of somewhat different form and dimensions were used. After the joints had been made, (taking care to keep the test-piece axial) and allowed to set, they were tested in a specially adapted Denison testing-machine. Determinations have been made both in tension and in shear.

Relation of Joint Strength to Thinness of Layer of Adhesive

In the previous communications many isolated data have indicated that the thinnest layers of adhesives give the strongest joints and this is confirmed by the preliminary study below. The best joints are obtained where the layer of adhesive is as thin as possible provided always that after drying or setting they are perfectly continuous and completely in contact with both the surfaces to be united. Where solvents are employed it is often necessary to use double or triple coatings in order to fulfill these conditions. In the present work however no solvents were involved.

Experiment 1. Aluminium and a proprietary shellac adhesive. A cylindrical stick of the cement of the same diameter as the test pieces was cut into slices of different thicknesses for use in comparative experiments. Each slice was allowed to stick to a hot metal test piece and when this had cooled the other half of the test piece was heated and applied. With all but the thinnest slices the central adhesive layer was left unmelted. The results are collected in Table I.

It is a difficult matter to examine where rupture begins; but as far as these and many other tension tests are concerned, an inspection of the fractured joints nearly always reveals a final breakdown of both adhesive and adhesion: and of these failure of the adhesive itself seems to predominate. Where failure of adhesion preponderated the explanation indicated by *ad hoc* experiments was that the temperature of the test pieces had been somewhat lower than usual during the preparation of the joint. It has to be remembered that the adhesive here used is not a substance of definite melting point, and

TABLE I

Relation of joint strength to thickness

Tension tests: aluminium and a commercial shellac adhesive

Thickness of adhesive (ins.)	Joint strength (lbs./sq. in.)	Time of setting (days)	Rate of loading (lbs./sq. in./sec.)
Usual*	2250	Several days.	Less than 38
0.04	750	6	25
0.05	500	1	25
0.08	350	8	21
0.13	400	8	(25)
0.17	350	10	21

*The adhesive film melted completely and the metal pieces were pressed together by hand.

that unless the metal test-pieces are hot enough no strong joint is possible between metal and shellac.

Experiment 2. Nickel and the same shellac adhesive. In this experiment the whole of the adhesive was kept molten during the preparation of the joint, being kept in place by a rubber tube surrounding the test-pieces. The rubber is readily removed from the shellac. The average thickness of adhesive layer was measured roughly by means of a micrometer microscope and is recorded in Table II in micrometer divisions, each of which is approximately 0.00012 inches.

Failure of the adhesive itself seemed to predominate as in the first experiment, but some failure of adhesion even though slight, seemed always to occur. Out of nine tests (Table 2) with nickel surfaces, only one failure was

TABLE II

Relation of joint strength to thickness

Tension tests: nickel and the same shellac adhesive as for Table I

Temp. °C	Thickness of adhesive (arbitrary units)	Joint strength (lbs./sq. in.)	Rate of loading (lbs./sq. in./sec.)
17	Extremely thin*	3600	60
,,	,, ,,	3000	60
21	30	2430	60
17	90	2150	30
,,	100	2030	(30)
17	100	1950	33
21	150	1550	50
,,	400	1075	54
,,	400	1000	50

*Optically polished test-pieces, which had been used more than once.

mostly in adhesion, and this was probably due to a slightly lower temperature of the upper half of the test-piece when preparing the joint. The general form of the curve showing the relation between joint strength and thinness of adhesive layer is clearly indicated in Fig. 1.

In a previous paper[1] it was mentioned that a curve of similar form for the joint strength of polished metal surfaces held together by films of liquid down to only a few hundred molecules thick had been obtained in the National Physical Laboratory. Crow[2] obtained a strikingly similar curve for various thicknesses of lead-tin solder between copper surfaces. It is noteworthy that the greatest dependence of joint strength upon thinness of adhesive layer is shown in the very thinnest layers. For example in measurements at the National Physical Laboratory the greatest effect was shown in layers less than one millionth of an inch thick. This gives rise to two important practical

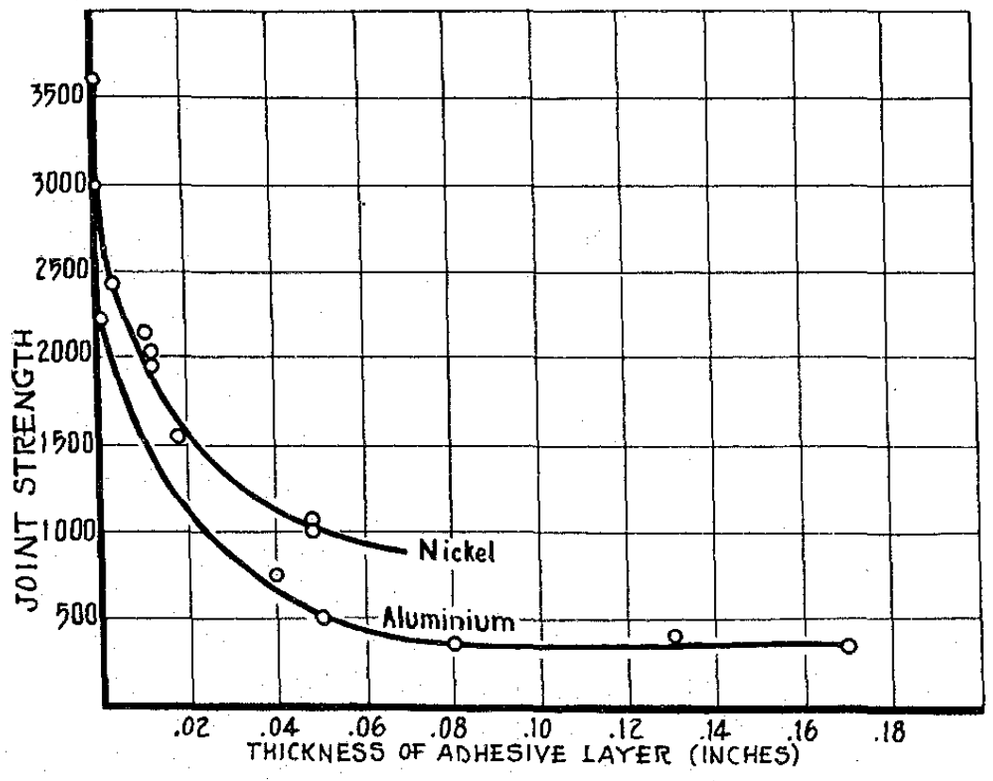


FIG. 1
Relation between joint strength and thinness of layer of adhesive

difficulties. In the first place, the effect is largest, and of the greatest theoretical interest, just in the regions where the practical difficulties of controlling and measuring the thinness of the film are greatest. In the second place it follows that if serious fluctuations are to be eliminated the thickness of adhesive layer must always be measured and taken into account. This has not been done either in our previous papers or in the general comparison of the adhesives studied in the second half of this paper, although a beginning has been made in subsequent work by designing a test piece in which such precision measurements have been shown to be possible. With thick films, that is those more than a tenth of an inch thick, the effect of thickness seems to become unimportant. It is seen in Fig. 1 that for each film of definite thick-

[1] Proc. Roy. Soc., **113** A, 617 (1927).
[2] J. Soc. Chem. Ind., **43**, 65-70 (1924).

ness between nickel and aluminium surfaces respectively the joint strength is always greater with the nickel than with the aluminium.

Experiment 3. Rubber solution between surfaces of mild steel. Confirmatory experiments have incidentally been obtained when showing that double and multiple coating is not advantageous in any "specific joint" between smooth surfaces provided that the first coating completely fills the space between the metal surfaces. Rubber solution was applied in successive coatings to steel surfaces and each coating allowed to dry before uniting the surfaces with a final coating. When the number of such coatings in four series of experiments was 2, 3, 5 and 8 respectively the mean of the two highest values for the joint strength in tension in each case was 300, 283, 160 and 115 lbs./sq. in.

Experiment 4. Sealing wax and Japan wax between optically polished steel surfaces. In experiments with steel surfaces optically polished at the National

TABLE III

Joint strengths in tension (maximum values found, lbs./sq. in.) using adhesives between metal surfaces

Adhesive	Nickel	Steel	Cast iron	Copper	Brass	Aluminum	Tin	Lead
Shellac creosote[1]	4000	4600		4000		1700	900	
Sealing wax	3150	3250[2]	3150	3000	2400	2200	1950	1000
Marine glue	1550	1600	(450)	1650				
Pitch	1540	1850		1350	1200	1200		
Phenol formaldehyde[3] (dried 6 days)	1300	(200)			2300	(500)		
Phenol formaldehyde (dried 14 days)[4]	1900	2500	1050		1500	1500	500	
Phenol formaldehyde (dried 5 days)	800	1300		1300	900	700		
Coumarone resin	1600	1800	1950[5]	1700	1600	1600		
Ester gum		1400	850	1450	1650[5]	1200	950	500
Guaiacum resin	1350			1400		950	850	
Gum Dammar	1050	(500)	900	800	950	600		
Carnauba wax				800		680	880	
Japan wax		(1300)[6]		490		460	540	430
Paraffin wax				300	250	320		
" " (set 5 days)				450		550	400	400
" " (" 6 ")[7]				450		300	450	400
$C_{26}H_{54}$ (set 2-3 days)[8]				420		370	370	250

[1] Supplied by Sir H. Jackson and containing the following parts by weight: hard shellac 50, creosote 5, ammonia 0.5, turpentine 2.
[2] This is the highest of four values, viz., 3250, 3100, 3000, 2550; the single experiment with optically polished surfaces gave nearly 3500.
[3] Commercial liquid.
[4] Fusible resin.
[5] Very thin film.
[6] Between optically plane surfaces, failure wholly within the Japan wax.
[7] From Scottish shale.
[8] Synthetic normal saturated paraffin of crystal spacing 37·75 Angström units.

Physical Laboratory, exceptionally thin and therefore strong films were obtained, stronger than those obtainable with any ordinary polished surfaces of metal. Similarly McBain and Hopkins (l.c.) obtained with shellac creosote cement between optically polished nickel surfaces a tensile strength of no less than 6400 lbs./sq. in. In all cases the failure was within the adhesive layer and not between metal and adhesive. The results are given for comparison in Table III.

Tension on Tests: Various Adhesives between Metal Surfaces

In order to provide further comparative data towards our survey of the strength of various adhesives with typical materials the measurements summarised in Table III have now been performed. The results are arranged in the order of the metals nickel, steel, cast iron, copper, brass, aluminium, tin and lead which is the order of the internal pressure, tensile strength, elasticity and (in reverse order) compressibility and atomic volume. To save space maximum values only are given in the table although usually three or four separate tests were made. A mixture of equal amounts of shellac and phenol formaldehyde resin between cast iron surfaces gave a value of 1000 lbs./sq. in. which is much lower than that obtained with either ingredient separately. Thicker films gave much lower values still. A series of experiments with beeswax showed that it was distinctly weaker than paraffin wax.

Although the general trend of the results is in agreement with the order of the metals as given, there are many exceptions and the effect seems to disappear with the weakest adhesives. Some of the many discrepancies in the table are however to be ascribed to the lack of strict comparability between the various tests. For example, metals are not equally corroded and the highest results are obtained where there is no corrosion. McBain and Hopkins found that where corrosion was extensive the rule as to the order of the metals broke down. Another example is provided by guaiacum resin where if only those joints are compared in which failure took place solely in adhesion between metal and adhesive the results for nickel, copper, aluminium and tin are without exception in the predicted order; namely, 1100, 1050, 950 and 850 lbs./sq. in. Likewise, with coumarone resin and phenol formaldehyde resin the low result with nickel can be attributed to the corrosion which occurred. With the waxes failure is mostly within the wax itself; in such cases one would expect to find the influence exerted by the various metals only with the thinnest films. Paraffin wax was found to be extremely brittle. The marine glue tended to segregate and likewise became brittle after long storage. In testing the strongest adhesives the elastic limits of such metals as tin and lead are reached or exceeded, a fact which must influence joint failure. Attention may be directed to pitch as an inexpensive ingredient for use in adhesives.

In Table IV are collected the results obtained with adhesives between metal test pieces when the joints were broken in shear. Here again the test pieces were in the form described in previous papers.

TABLE IV

Joint strength in shear (maximum values found, lbs./sq.in.) using adhesives between metal surfaces

Adhesive	Nickel	Steel	Cast iron	Copper	Brass	Aluminum	Tin
Shellac reosote	4900	3500		4900		2450	1050
Sealing wax	2900	2500	2750	2300	2350	2100	
Phenol formaldehyde* (set 5 days)	1100	1500		1200	850	1000	450
Gum Dammar		700	850	650	700	1000	
Paraffin wax (set 12 days)				250		250	200
Paraffin wax** (set 1 day)				200		50	200

*Commercial fusible resin.
**Result with lead 200 lbs./sq. in.

It is interesting to note that in general the joint strength in shear is the same as in tension.

Summary

1. The results obtained from our studies of adhesion have been briefly reviewed.

2. The thinner the layer of adhesive the stronger the joint. The effect of thickness is not appreciable with very thick films but is rapidly increasing when the thinnest possible films are studied.

3. Data are provided which show the adhesive power of various materials for metals.

4. On the whole the rule is confirmed that the parallelism exists between the strength of a joint between smooth metallic surfaces and the mechanical and intrinsic properties of the metals themselves.

University of Bristol, England
and Stanford University, California.
July 2, 1927.

GIBBS ON EMULSIFICATION

BY WILDER D. BANCROFT AND C. W. TUCKER

The modern theory of emulsification is contained implicitly in Gibbs, though it has not been very easy to find it there. All references are to "The Scientific Papers of J. Willard Gibbs," Vol. I (1906).

The best starting point is the section on the possible formation, at the surface where two different homogeneous fluids meet, of a fluid of different phase from either, because that is exactly what happens when oil and a soap solution are brought in contact. Gibbs is using the word 'homogeneous' in the popular sense and he is not making any assumption as to soap being dispersed or dissolved in water. "Let A, B, and C be three different fluid phases of matter, which satisfy all the conditions necessary for equilibrium when they meet at plane surfaces. The components of A and B may be the same or different, but C must have no components except such as belong to A or B. Let us suppose masses of the phase A and B to be separated by a very thin sheet of the phase C. This sheet will not necessarily be plane, but the sum of its principal curvatures must be zero. We may treat such a system as consisting simply of masses of the phases A and B with a certain surface of discontinuity, for in our previous discussion there has been nothing to limit the thickness or the nature of the film separating homogeneous masses, except that its thickness has generally been supposed to be small in comparison with its radii of curvature. The value of the superficial tension for such a film will be $\sigma_{AC} + \sigma_{BC}$, if we denote by these symbols the tensions of the surfaces of contact of the surfaces A and C, and B and C respectively. This not only appears from evident mechanical considerations, but may also be verified by equations (502) and (93), the first of which may be regarded as defining the quantity σ. This value will not be affected by diminishing the thickness of the film, until the limit is reached at which the interior of the film ceases to have the properties of matter in mass. Now if $\sigma_{AC} + \sigma_{BC}$ is greater than σ_{AB}, the tension of the ordinary surface between A and B, such a film will be at least practically unstable. (See page 240). We cannot suppose that $\sigma_{AB} > \sigma_{AC} + \sigma_{BC}$ for this would make the ordinary surface between A and B unstable and difficult to realize. If $\sigma_{AB} = \sigma_{AC} + \sigma_{BC}$, we may assume, in general, that this relation is not accidental, and that the ordinary surface of contact for A and B is of the kind which we have described," p. 258.

Gibbs is quite clear that we must recognize different surfaces tensions on the two sides of the film. When it was suggested, some years ago, that the type of emulsion was determined by the difference in the surface tensions on the two sides of the film,[1] some people[2] objected that a monomolecular film

[1] Bancroft: J. Phys. Chem., 17, 515 (1914).

[2] Harkins, Davies and Clark: J. Am. Chem. Soc., 39, 593 (1917); Finkle, Draper and Hildebrand: 45, 2781 (1923).

can not have two surface tensions. Hildebrand says that "the idea of a film with two surface tensions, one on the oil side and another on the water side, is rather disconcerting, for no one is likely to measure separately the surface tensions on two sides of an interface, and we have evidence furthermore, that the emulsifying agent may form films at the interface which are but one molecule thick."

This is based on a misunderstanding. In principle, the minimum thickness of the film in an emulsion is three molecules, one each of A, B, and C. It is simpler, however, to emphasize the fact, as Gibbs does, that there are two surfaces and consequently two surface tensions.

We cannot agree with Gibbs either in the statement that σ_{AB} cannot be larger than $\sigma_{AC} + \sigma_{BC}$ or in the reason given that the ordinary surface between A and B is unstable and difficult to realize. The conditions for a film spreading between A and B is that $\sigma_{AB} > \sigma_{AC} + \sigma_{BC}$ and the ordinary surface between A and B is unstable, because that is what makes the formation of C possible and necessary.

Disregarding this for the moment, we wish to show that Gibbs comes out, at least indirectly, with the result that A is emulsified in B, in case $\sigma_{AC} > \sigma_{BC}$. To do this, we must start with a relation for the superficial tension. "With the aid of (23), the remaining condition of equilibrium for contiguous homogeneous masses is found, viz.,

$$\sigma\,(c_1 + c_2) = p' - p'', \qquad (25) \quad [500]$$

where p', p'' denote the pressures in the two masses, and c_1, c_2 the principal curvatures of the surface. Since the equation has the same form as if a tension equal to σ resided at the surface, the quantity σ is called (as is usual) the *superficial tension* and the dividing surface in the particular position above mentioned is called the *surface tension*," p. 366.

Gibbs does not seem to define anywhere what he means by the pressures in the two masses and it is not a conception which is ordinarily familiar to the chemist. If we consider a water fog in the absence of air, the pressure in the vapor phase is the pressure of the water vapor. The pressure on the liquid drops is this pressure plus the pressure which has made the drops spherical and which is a function of the surface, tension, internal pressure, or what you will. If we substitute in (25) the radius of a spherical drop for the radii of curvatures, we get

$$2\,\sigma = (p' - p'')r. \qquad (27) \quad [522]$$

When the surface of discontinuity is plane, $p' = p''$, p. 226, which means that the force of gravity has neutralized the surface tension effect.

"In order that a thin film of the phase C may be in equilibrium between masses of the phases A and B, the following equations must be satisfied:—

$$\sigma_{AB}\,(c_1 + c_2) = p_A - p_C$$
$$\sigma_{BC}\,(c_1 + c_2) = p_C - p_L$$

where c_1 and c_2 denote the principal curvatures of the film, the centers of positive curvature lying in the mass having the plane A. Eliminating c_1 and c_2 we have

$$\sigma_{BC}\,(p_A - p_C) = \sigma_{AC}\,(p_C - p_B)$$

or

$$p_C = \frac{\sigma_{BC}p_A + \sigma_{AC}p_B}{\sigma_{BC} + \sigma_{AC}} \qquad (571)$$

It is evident that if p_C has a value greater than that determined by this equation, such a film will develop into a larger mass; if p_C has a less value, such a film will tend to diminish. Hence, when

$$p_C < \frac{\sigma_{BC}\,p_A + \sigma_{AC}\,p_B}{\sigma_{BC} + \sigma_{AC}} \qquad (572)$$

the phases A and B will have a stable surface of contact," p. 572.

So far as we can find, Gibbs does not anywhere state definitely that $\sigma_{AC} > \sigma_{BC}$, apparently because it did not occur to him that anybody could question it. The result folllows indirectly from the discussion by Gibbs of the work, W, "which would be required to form (by a reversible process) a heterogeneous globule in the interior of a very large mass having initially the increment of energy of the system when the globule is formed without change of the entropy or volume of the whole system or of the quantities of the several components," p. 255.

"By equation (553) which may be written

$$W = \sigma s - (p' - p'')v', \qquad (559)$$

we see that the work W consists of two parts, of which one is always positive, and is expressed by the product of the superficial tension and the area of the surface of tension, and the other is always negative, and is numerically equal to the product of the difference of pressure by the volume of the interior mass. We may regard the first part as expressing the work spent in forming the interior mass.[1] Moreover the second of these qualities, if we neglect its

[1] To make the physical significance of the above more clear, we may suppose the two processes to be performed separately in the following manner. We may suppose a large mass of the same phase as that which has the volume v′ to exist initially in the interior of the other. Of course it must be surrounded by a resisting envelope, on account of the difference of the pressures. We may, however, suppose this envelop permeable to all the component substances, although not of such properties that a mass can form on the exterior like that within. We may allow the envelop to yield to the internal pressure until its contents are increased by v′ without materially affecting its superficial area. If this be done sufficiently slowly, the phase of the mass within will remain constant. (See page 84). A homogeneous mass of the volume v′ and of the desired phase has thus been produced, and the work gained is evidently $(p' - p'')v'$.

Let us suppose that a small aperture is now opened and closed in the envelop so as to let out exactly the volume v′ of the mass within, the envelop being pressed inwards in another place so as to diminish its contents by this amount. During the extrusion of the drop and until the orifice is entirely closed, the surface of the drop must adhere to the edge of the orifice, but not elsewhere to the outside surface of the envelope. The work done in forming the surface of the drop will evidently be σs or $3/2\,(p' - p'')v'$. Of this work, the amount $(p' - p'')v'$ will be expended in pressing the envelop inward and the rest in opening and closing the orifice. Both the opening and the closing will be resisted by the capillary tension. If the orifice is circular, it must have, when widest open, the radius determined by equation (550).

sign, is always equal to two-thirds of the first, as appears from the equation (550) and the geometrical relation $v' = \frac{1}{3}$ rs. We may therefore write

$$w = \tfrac{1}{3}\sigma s = \tfrac{1}{2}(p' = p'')v', \text{" p. 257.} \qquad (560)$$

If we consider two large but thin masses of oil and aqueous soap solution, the surfaces of discontinuity will be practically plane and therefore all the pressure will be equal and the pv^1 terms will drop out. If we are merely considering the tendency of the soap film to bend one way or the other, there is no change in its volume and the factor determining the tendency to curve one way or the other will be the relative magnitudes of $\sigma_1 s_1$ and $\sigma_2 s_2$. While the surfaces are plane, $s_1 = s_2$ and therefore the center of positive curvature will be on the side having the larger sigma. In other words, if $\sigma_1 > \sigma_2$, the liquid corresponding to σ_1 will be the internal phase and the liquid corresponding to σ_2 will be the external phase. In the nomenclature used by Gibbs, this means that $\sigma_{AC} > \sigma_{BC}$. That Gibbs knew that σ_{AC} is not in general equal to σ_{BC} is shown by the drawing on p. 260.

There remains the question why Gibbs considered that $\dfrac{\sigma_{AB}}{\sigma_{AC} + \sigma_{BC}}$ cannot be greater than unity, p. 258. The only explanation we can offer for this apparently inaccurate statement is that Gibbs was only considering, without so saying, the case in which the new film does not cover the whole of the surface between A and B. If we were to take oil and a soap solution so dilute that all the soap in it would not suffice to make a monomolecular layer at the surface between A and B, we should then get a circular soap film with A and B in direct contact outside of that. For this case it is true that $\sigma_{AB} = \sigma_{AC} + \sigma_{BC}$. In confirmation of this is a statement on p. 261 that "it should however be observed that in the immediate vicinity of the circle in which the three surfaces of discontinuity intersect, the physical state of each of these surfaces must be affected by the vicinity of the others."

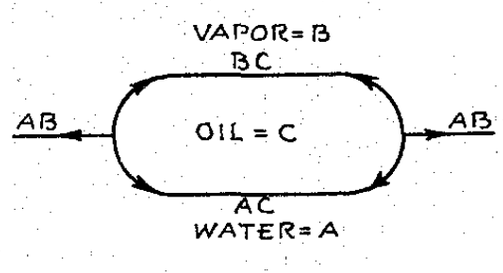


FIG. 1

It is easier to see some of the relations if they are presented graphically and it is easier to believe them if they can be shown experimentally. In Fig. 1 let A be liquid water, C be an oil which is less dense than water, and B the vapor phase. The three surface tensions, σ_{AB}, σ_{AC}, and σ_{BC}, and the directions in which they act are indicated by the three arrow-heads at the two ends of the drop C. If $\sigma_{AB} < \sigma_{AC} + \sigma_{BC}$ the drop C will draw up and become more nearly spherical. If, at the same time, $\sigma_{AC} < \sigma_{BC}$, the drop will be pushed

down into the water because the surface BC will shorten relatively to the surface AC. If $\sigma_{AC} > \sigma_{BC}$, the drop will stand up on the surface of the water.

If $\sigma_{AB} > \sigma_{AC} + \sigma_{BC}$, the drop will spread out as a film over the surface of the water, the oil covering the whole surface of the water. If there is not enough oil to cover the surface of the water one molecule thick, it will spread until that thickness is reached and will then stop. Under these conditions we shall have $\sigma_{AB} = \sigma_{AC} + \sigma_{BC}$. This is apparently the case that Gibbs had in mind and is the case that has been studied in detail by Langmuir, Adam, and others in recent years.

We are more interested in the case in which there is enough oil to cover the whole surface with a thin film of adsorbed oil. This film will not necessarily have the properties of oil in mass. We have now the problem of an adsorbed oil film which we will call C′ in contact with the vapor B and the oil drop C, between liquid water, the liquid water being no longer in direct contact with the vapor phase. We have therefore to consider whether $\sigma_{BC'} > \sigma_{BC} + \sigma_{CC'}$ or whether $\sigma_{BC'} < \sigma_{BC} + \sigma_{CC'}$. At first sight it seems obvious that the surface tension $\sigma_{CC'}$ between free and adsorbed oil would be zero. If that were the case $\sigma_{BC'}$ would unquestionably be greater than σ_{BC} and further additions of oil must spread over the water.

Under all circumstances $\sigma_{BC'} < \sigma_{AB}$. If $\sigma_{CC'}$ does not approximate zero, for some at present unknown reason connected with adsorption, it might happen that $\sigma_{BC'}$ would be less than $\sigma_{BC} + \sigma_{CC'}$, in which case an additional amount of oil would not spread out as a film; but would form drops on the oiled surface of the water. This actually happens with oleic acid and water, also with many other oils and water.

One of us has previously given[1] a somewhat different way of looking at this subject. "If oil is adsorbed by water, it wets the water and spreads over the surface. Now the adsorbed layer may be very thin, not over $2\mu\mu$ in some cases. At greater thicknesses there is nothing to prevent the oil tearing loose from the oiled surface of the water and drawing up into drops under the influence of surface tension. This has been commented on by Rayleigh[2] and by Budgett.[3] The first portion of oil spreads over the water because it is adsorbed and held by the water. The second portion of oil flows out over the oiled surface, but is instable because the same mass of oil would have a smaller surface if present in drops, and still more so if present in a single drop. The excess oil, therefore, draws up into one or more drops, depending upon conditions, thereby leaving bare, oiled surfaces. The several drops will coalesce into one large one if brought into contact. If more oil is added, the drops become larger and finally form so large a drop that, under the influence of gravity, it covers the whole surface of the water and becomes a liquid layer of free oil. From this way of looking at it, we see that the phenomenon must be general, and so it is. Budgett[4] found that it was quite impossible to get a thin con-

[1] Bancroft: "Applied Colloid Chemistry," 96 (1926).
[2] "Scientific Papers," **3**, 424 (1902).
[3] Proc. Roy. Soc., **85**, 25 (1911).
[4] Proc. Roy. Soc., **85A**, 30 (1911).

tinuous film of kerosene or water on the surface of steel blocks. Microscopic examination showed that the applied films were not continuous membranes, but that the liquid collected into small drops. This is undoubtedly exactly like Rayleigh's experiment. On the surface of the wetted steel the kerosene or water gathered into small drops. With different liquids we should expect to find the drops first forming when the films reached different thichnesses. This has been noted by Hardy,[1] who found that the thickness of the oil film varies from 2-200$\mu\mu$ with different oils. With one sample of oil there was no spreading at all."

The case of two liquid layers with a film between them is a very simple case. We can use Fig. 1 if we now let A = water, B = an oil which is less dense than water, and C = the film, which may be a soap or any other suitable material. The postulate that the oil shall be less dense than water is of course not essential to the theoretical development. The same reasoning would apply to the other case if we drew another figure with B below and A above.

For C to form a film it is essential that $\sigma_{AB} > \sigma_{AC} + \sigma_{BC}$. If $\sigma_{AC} > \sigma_{BC}$, the film C will tend to become convex towards the B phase because this shortens the surface AC relatively to the surface BC. In other words, water will tend to be emulsified in oil. If $\sigma_{AC} < \sigma_{BC}$, the film C will tend to become convex toward the phase A because this shortens the surface BC relatively to the surface AC. In other words, oil will tend to be emulsified in water. We thus see that the sole factor determining the type of emulsion is the sign of the difference between σ_{AC} and σ_{BC}. This conclusion is contained implicitly in Gibbs and was formulated explicitly by the senior author more than a dozen years ago.

No really satisfactory experimental proof of this has ever been given. If one poured water and then oil into a test-tube or a beaker and added a sodium soap solution, the dividing surface should theoretically become concave or more concave as seen from above, while the dividing surface should theoretically become convex or more convex if a calcium soap were added instead of a sodium soap. This can be shown; but it is not a satisfactory experiment because there may be complications due to preferential wetting of the containing walls with the resultant effect on the form of the meniscus.

The junior author has developed an experimental technique, which seems to meet all reasonable requirements and to have rather interesting possibilities. Everybody is willing to admit that the flattening of a drop is a sign of a decreased surface tension, while the becoming more nearly spherical indicates an increased surface tension. The apparatus consists of a light-tight box, with an incandescent lamp inside and with a hole cut in the top to hold a watch glass. Water, a water solution, oil, or an oil solution is added to the watch-glass in sufficient quantity to give a practically level liquid surface and then a drop of oil solution, oil, water solution, or water is added carefully from a pipette. Since the added drop does not come in direct contact

[1] Proc. Roy. Soc., **86A**, 612 (1912).
[2] Bancroft: J. Phys. Chem., **17**, 515 (1914).

with the watch-glass, the disturbing factor of preferential adsorption by the glass appears to be eliminated. The following, preliminary, results have been obtained so far. With a sodium oleate solution addition of benzene causes the formation of a nearly spherical drop which is immersed somewhat in the soap solutiom. If a little lime water is added, the drop of benzene spreads out as a film over the water surface. A film is also formed if benzene is added to an aqueous solution of calcium oleate.

If one adds a drop of aqueous sodium oleate to a benzene layer, the drop forms a film at the bottom of the benzene layer, between it and the glass. On addition of more water, the new drop coalesces readily with the one at the bottom, forming a larger film. If one adds a drop of aqueous calcium oleate to the benzene layer, there is formed a convex drop on the watch-glass, which does not coalesce readily with a second drop. The difference in the two cases is quite striking and exactly like what it should be.

When olive oil is dropped on an aqueous sodium oleate solution, the oil stands up in a drop on the surface; but a drop of olive oil spreads out into a thin film if it is placed on an aqueous solution of calcium oleate. Although water is more dense than olive oil it is possible to keep a drop of water on the surface if it is placed there carefully. A drop of aqueous sodium oleate spreads on the surface of olive oil, while a drop of aqueous calcium oleate stands up very well. So-called pure olive oil spreads on a water layer, perhaps owing to the fatty acids in the oil. Addition of a drop of aqueous sodium oleate causes the film of olive oil to coagulate into drops.

A drop of benzene on a water layer does not spread appreciably. The first drop of oleic acid spreads on water but the second one does not. A drop of oleic acid dissolves in benzene. Addition of a drop of oleic acid and benzene to a water layer gives a drop and not a spreading film, showing that oleic acid does not cause the emulsification of water in benzene. The addition of water to benzene containing oleic acid, iodine or methanol is not as satisfactory an experiment as one would like because the water forms a film between the benzene and the glass even when the oleic acid, iodine, or methanol is not there. It might be urged that these benzene solutions tended to emulsify water in benzene but that this was more than counterbalanced by the effect of the glass. This argument can be met in several ways. If we go on adding water drop by drop, we shall reach a point where the glass surface is covered to a suitable thickness. If the benzene solution tends to emulsify water, the next drop should stand up, just as the first drop does in the case of aqueous calcium oleate. This does not happen. Further addition of water causes a continual increase in the thickness of the water film.

In an aluminum dish, water wets the metal less readily than it does glass and the drop flattens much more slowly. If the water drop is added to benzene in which enough iodine has been dissolved to give it a strong red color, the drop flattens more quickly than in pure benzene. A drop of water, about 2 mm in diameter, placed in contact with aluminum in pure benzene, showed

considerable curvature after standing for twelve hours. In benzene containing iodine, the drop was flattened appreciably after three hours, and much more so after twelve hours. The experiment is by no means as striking as one would like; but it appears that the interfacial tension between the water and benzene has been measurably decreased. A similar experiment, performed with a drop of water in a benzene-methyl alcohol medium, gave more positive results. The water drop dissolved alcohol until it finally rose to the surface of the benzene solution and spread out to form a thin layer. The longer diameter of this layer was approximately ten times the diameter of the original water drop. There was also a film of a water layer on the aluminum.[1]

Many people who have written on emulsions have confused two things which ought to be kept quite distinct: the factor determining the type of emulsion and some other property from which the type of emulsion can be perdicted. As has been shown, the factor determining the type of emulsion is the sign of the difference of surface tension between the two sides of the emulsifying film, the emulsified liquid being on the side of the higher surface tension. There are and there can be no exceptions to this. On the other hand, we have as yet no infallible method of predicting the type of emulsion from any other property of the system. The best one is still the one[2] proposed by the senior author in 1914. "The simplest way to emulsify oil in water is to add a water-soluble colloid which is adsorbed strongly at the interface, and the simplest way to emulsify water in oil is to add an oil-soluble colloid which is adsorbed strongly in the interface. As a matter of fact, this is the way in which almost all emulsions are made."

This formulation is applicable in the overwhelming majority of cases; but it does not cover the ground absolutely. Oleic acid is soluble in benzene and it is not peptized markedly by water.[3] One would therefore have expected it to emulsify water in benzene; but it actually emulsifies benzene in water. Holmes[4] has emulsified ether in water with iodine and benzene in water with methanol. Not one of these three cases could have been predicted.

It is probable that the essential formulation—which we owe to Briggs—is that we get oil-in-water if the emulsifying agent at the interface is chiefly in the water phase and water-in-oil if the emulsifying agent at the interface is chiefly in the oil phase. On this assumption it will be necessary to show that the surface adsorption of oleic acid by water is so great that the oleic acid passes chiefly into the water side of the interface. This has not yet been done, partly because nobody has yet tried to do it. When it has been done, it will be necessary to find some convenient way of identifying such cases. Methanol with benzene and water is even more unexpected because it is miscible in all proportions both with benzene and with water. There must be some rather extraordinary and quite unexpected surface adsorption in this case.

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[1] These last experiments were done by Mr. H. W. Rogers.

[2] Bancroft: "Applied Colloid Chemistry," 262 (1921).

[3] Finkle, Draper and Hildebrand: J. Am. Chem. Soc., **45**, 2781 (1923).

[4] J. Am. Chem. Soc., **47**, 323 (1925); "Colloid Symposium Monograph," **2**, 135 (1925).

If Briggs' point of view is right, as seems probable, there is a very interesting corollary as regards oleic acid. If we substitute other organic liquids for benzene, we shall probably find one or more which will cut down the adsorption of oleic acid by water, in which case we shall have the oleic acid emulsifying water in the organic liquid. An organic liquid of intermediate properties would give no emulsion. What may be a case of this sort has been studied by Seifriz[1] with carefully fractionated petroleum distillates.[2] "When emulsified with water and casein, those of less than 0.820 specific gravity form fine, stable, oil-in-water emulsions; those of 0.828 specific gravity form coarse and poorly stable oil-in-water emulsions; those of 0.828 to 0.857 specific gravity form no emulsion at all; those of 0.857 to 0.869 specific gravity form coarse to medium, poorly to moderately stable, water-in-oil emulsions; while those of 0.869 to 0.895 specific gravity and above form fine, stable emulsions of water in oil. Of course the specific gravity has nothing in itself to do with the reversal of type. That is put in to make the problem more difficult. There are apparently only two possibilities. Either the petroleum distillates contain an emulsifying agent which tends to emulsify water in oil and the amount of this hypothetical substance increases in the distillates of higher specific gravity, or the petroleum distillates of higher specific gravity peptize casein more readily than water does.[3] It would have been a simple matter to have tested these two possibilities; but Seifriz was apparently not interested in finding an explanation for his results. His mission was to collect data. Dodd[4] states that asphalt is most frequently the emulsifying agent in petroleum emulsions; but that does not seem very probable in the distillates as obtained by Seifriz." Ddecreasing the peptizing power of water for oleic acid is a possible method of making oleic acid peptize water in benzene."

Harkins[5] and Hildebrand[6] have developed a wedge theory of emulsification based on the orientation of molecules at the interface. They postulate that the colloidal emulsifying particles must have both polar and non-polar groups upon their surfaces so as to be adsorbed at the interface. It is not clear how this will apply to carbon. "If the polar groups, in the water, occupy more space than is necessary for the closest packing of the hydrocarbon chain, the latter can be packed more closely if the film is convex on the water side. It is obvious that the direction and degree of curvature, if this hypothesis is correct, should vary, first, with the atomic volume, and second, with the number of hydrocarbon chains attached to a single metal atom, according to its valence. A zinc soap, for example, with two hydrocarbon chains per atom of metal, crowded together in the oil phase, should tend to make the

[1] J. Phys. Chem., **29**, 587 (1925).

[2] Bancroft: "Applied Colloid Chemistry," 356 (1926).

[3] [This should now read that casein goes chiefly into the petroleum side of the interface with the distillates of higher specific gravity.]

[4] Chem. Met. Eng., **28**, 249 (1923).

[5] Colloid Symposium Monograph, **2**, 141 (1925); Harkins, Davies and Clark: J. Am. Chem. Soc., **31**, 549 (1917).

[6] J. Am. Chem. Soc., **45**, 2780 (1923); Bogue's "Theory and Application of Colloidal Behavior," 212 (1924).

film convex towards the oil, while an aluminum soap, with its three hydrocarbon chains in the oil, should give still more curvature towards the water and hence relatively stable emulsions of water in oil."

It has already been pointed out[1] that "this hypothesis might come to grief with basic aluminum acetate as emulsifying agent; but a more serious objection is the one raised by Seifriz[2] that the wedge hypothesis demands a monomolecular film or at least a membrane of the order of molecular dimensions while, as a matter of fact, the membranes surrounding the dispersed drops in many emulsions are optically visible. Also, the effect of the wedge would be important only in case the molecules of the emulsifying agent are packed closely at the interface, which is not necessarily the case. What Harkins and Hildebrand really mean is that we get oil-in-water if the oriented molecule of the emulsifying agent is chiefly in the water phase and the water-in-oil if the oriented molecule is chiefly in the oil phase. If worded in this way, the wedge hypothesis ceases to be an independent hypothesis and becomes a special case in the general theory."

As a matter of fact both Harkins[3] and Hildebrand[4] have modified their original views a good deal. It is perfectly legitimate to discuss the relative merits of the peptization and the wedge hypotheses if one so wishes. It shows a confusion of mind to discuss the relative merits of the surface tension theory and the wege hypothesis, as done by Mead and McCoy,[5] because the first is true irrespective of whether the second is or is not. Their formulation of both points of view leaves much to be desired.

"It is generally accepted that interfacial tension lowering and emulsification power are very closely related. Some[6] go so far as to say that interfacial tension lowering is the controlling factor in emulsification. This much is certain, that those substances which lower the surface tension of water do also act as emulsifying agents for oil in water. The mechanism by which the stabilization occurs has been variously explained. Thus Bancroft[7] has postulated a film of molecules of emulsifying agents around the globules of dispersed phase. This film may be considered as being held in position by the forces of adsorption. By lowering the surface tension on the water side of the interface, the film is so curved that it eventually actually encloses a drop of oil and prevents its coalescence with another similarly enclosed drop.

"The oriented wedge theory of Langmuir-Harkins[8] is of a different type altogether. It has as its main postulate the polar nature of the substance which acts as emulsifying agent. This results in one part of the molecule

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[1] Bancroft: "Applied Colloid Chemistry," 355 (1926).
[2] J. Phys. Chem., **29**, 594 (1925).
[3] Proc. Nat. Acad. Sci., **11**, 631 (1925).
[4] J. Phys. Chem., **31**, 1578 (1927).
[5] Colloid Symposium Monograph, **4**, 44 (1926).
[6] Hillyer: J. Am. Chem. Soc., **25**, 513 (1903); White and Marden: J. Phys. Chem., **24**, 617 (1920).
[7] "Applied Colloid Chemistry," 261 (1921).
[8] Bogue's "The Theory and Applications of Colloidal Behavior," **1**, 142, 210 (1924).

being strongly attracted by, and imbedded in, the water, while another is equally strongly held in the oil phase. This results in an extremely strong bond between the two phases." It is not clear why this last is not also a case of a film of molecules of emulsifying agent, around the globules of the dispersed phase and held in position by the forces of adsorption.

Rideal's[1] treatment is even worse, because he ignores the surface tension relations completely. "Thus the type of emulsion formed depends essentially on the relative cross-section areas of the non-polar and polar portions of the emulsifying agent. Furthermore if we represent diagrammatically the cross-section of two soap molecules in juxtaposition to one another at the interface of an oil-in-water emulsion as follows [cut not reproduced], it is clear that the curvature of the interface or fineness of the emulsion is dependent on three factors, the cross-section of the head or polar end, and the -COONa group, the cross-section of the non-polar or hydrocarbon chain and the length of the molecule."

The general conclusions of this paper are as follows:—

1. The modern theory of emulsification was given at least inplicitly by Gibbs.

2. Gibbs recognized explicitly that a film has two surfaces and will therefore have two surface tensions if in contact with the different phases.

3. Gibbs has shown a drawing in which it is recognized that these two surface tensions are not necessarily equal.

4. The film will tend to curl toward the side having the higher surface tension.

5. In all emulsions the dispersed liquid is on the side of the film having the higher surface tension. There is no exception to this generalization and there can be none.

6. The low interfacial tension for two liquids, which is what people usually measure is the difference between the surface tensions on the two sides of the dividing surface.

7. In many cases the surface tension between adsorbed oil and oil in mass does not become zero. This makes it possible for oleic acid, for instance, to draw into drops on a surface of water previously wetted by oleic acid.

8. An experimental technique has been developed to show that the surface tension of the emulsifying film is higher on the side of the emulsified liquid. It is possible that an absolute measurement could be made by this method.

9. At present there is no absolute method of predicting the type of emulsion from any other property than the surface tensions of the film. In most cases it is satisfactory to say that the liquid which wets or peptizes the emulsifying agent the more readily, is the dispersing medium; but this generalization in this form breaks down for benzene, oleic acid and water, for benzene,

[1] "An Introduction to Surface Chemistry," 113 (1926).

iodine and water, for benzene, methanol and water, and, doubtless, for many other cases.

10. Benzene, oleic acid and water can be brought into line by postulating that water adsorbs oleic acid so strongly that the oleic acid is chiefly on the water side of the interface (Briggs); but there is no independent experimental evidence of this as yet, and we do not know how to predict it.

11. It is possible, though not yet proved, that suitable additions to water might cut down the adsorbing power of water for benzene so much that oleic acid would peptize the aqueous solution in benzene.

12. By substituting other organic liquids for benzene, by a suitable change of temperature, or by a combination of both, it might be possible to increase the peptizing or solvent action of the organic liquid to oleic acid to such an extent that an emulsion of water on the organic liquid would be formed. If so, an intermediate set of conditions would make both types of emulsions instable. It is possible, though not yet proved, that something similar to this happened with the petroleum distillates, casein, and water studied by Seifriz.

Cornell University.

15A-1481

A STUDY OF ANNEALING EFFECTS OF CERTAIN COPPER-NICKEL-ALUMINIUM-MANGANESE ALLOYS*

BY LYMAN J. WOOD

The desirability of being able to predict the properties of an alloy before it is made up has been repeatedly emphasized. While the sum total of knowledge of properties of alloys has increased and the number of valuable alloys has been greatly multiplied, theories correlating their composition and properties are, to a large extent, still wanting. However, in view of our increasing knowledge of the crystalline habits of metals, space lattice dimensions and the properties of intercrystalline compounds, solid solutions and eutectic mixtures, the problem does not appear entirely without hope.

In a former paper[1] it was pointed out that valuable binary alloys are the exception rather than the rule; and data, obtained from three alloy systems of the ternary type, were submitted which indicated in a general way that, (a) the composition range of valuable alloys in a given ternary system is quite limited, (b) for the most part these valuable ternary alloys are likely to be solid solutions of one kind, (c) the addition of a small amount of a fourth metal may have a very profound influence upon the properties of the alloys. It was also suggested that the beneficial or deleterious effect of this fourth metal on the ternary depended upon whether or not mutual solid solubility was helped or hindered. It has been the purpose of this work to investigate more thoroly the influence of a fourth metal, manganese, on the ternary system copper-nickel-aluminium.

Plan of Work

According to the plan followed the sand-cast Cu-Ni-Al-Mn alloys were annealed and their properties after annealing compared with those before annealing. The properties examined were density, corrosion resistance and microstructure before and after annealing. Also a careful microscopic study of some of the alloys which contained no manganese and some which had been cast in chill molds was carried out and a comparison made with sand-cast alloys. It was hoped that the data obtained would define more clearly the influence of manganese on the ternary copper-nickel-aluminium and perhaps offer an explanation for this influence. The alloys used were the copper-nickel-aluminium-manganese alloys described in the above mentioned paper, the specimens which had formerly been used for acid corrosion tests being the parts used.

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*From the Chemistry Laboratory of Saint Louis University.

[1] Correlation of Physical and Chemical Properties in Alloys of the Ternary Type, by L. J. Wood and S. W. Parr. Preprint of the American Institute of Chemical Engineers, Dec. 2 (1925).

Method of Annealing

The annealing process was carried out under the author's direction by Mr. N. L. Michener[1]. The alloy specimens were first placed in a wire-wound electric furnace and held at a temperature of 500° C for seven days. Subsequent tests indicated that but little change in properties had occurred so the alloys were again annealed at 800° C for five days. The temperature, which was measured by means of a thermocouple, did not vary more than plus or minus ten degrees during the annealing periods.

Density Determinations

Density determinations of the sand-cast alloys before and after annealing have been very carefully made, values being obtained which are accurate to plus or minus .5 milligram. The method used was that described by Egerton and Lee[2] which is a refinement of the ordinary displacement method for which the authors claim an accuracy of one in ten thousand. It was found possible to determine the density of the alloys under consideration to the fourth decimal place but the determination was very time-consuming and uncertain unless a large number of determinations were made. The metal specimens were weighed suspended in carbon tetrachloride on a balance sensitive to .02 or .03 milligrams. The temperature, which was the most difficult factor to control, was estimated to .002 or .003 degree centigrade by means of a small Beckmann thermometer. The average temperature coefficient of the density was determined and found to be about .00095 grams for one degree centigrade. This was used in correcting the density determinations to a constant temperature.

Corrosion Tests

The method of making the corrosion tests was identical with that used in the former work with these alloys. The metal specimens were allowed to remain quietly in the corroding medium during the entire test period. The corroding agent in all cases was 4 N nitric acid, either at room temperature or at 60° C. The amount of corrosion was calculated in milligrams loss in weight per square centimeter of surface exposed.

Statement of Results

In Table I is shown the compositions of the sand-cast alloys and their densities before and after annealing. In all but three cases, alloys 109, 127, and 137, there was a decrease in density upon annealing. The change in density of alloy number 127 was not as large as the possible experimental variation, however, this small variation is believed to be due to a partial neutralization of two opposing tendencies rather than to no change, as will be pointed out below.

Table II shows the loss in weight in milligrams per square centimeter for each alloy before and after annealing when allowed to remain suspended in 4 N nitric acid at 60° C for one hour and at room temperature for four hours.

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[1] Unpublished Master's Thesis, Defiance College.

[2] Proc. Roy. Soc., **103** A, 487 (1923).

Two of the alloys, namely, numbers 127 and 137, which showed an increase in density also showed an increase in corrosion. The third alloy, number 109, which showed an increase in density showed only a slight change in the

TABLE I

Showing the Compositions of the Sand-Cast Cu-Ni-Al-Mn Alloys and their Densities before and after Annealing

	Composition of Charge					Density			
No.	Cu	Ni	Al	Mn	Ni/Cu	Before Annealing	After Annealing	Increase In Density	Decrease in Density
104	30	67	2	1	2.23	———*	8.5608		
105	29	64	6	1	2.23	8.1565	8.1486		.0079
106	29	66	4	1	2.28	8.3496	8.3437		.0059
108	29	67	3	1	2.31	8.4570	8.4498		.0072
109**	26.9	69.8	1.7	1	2.58	8.3204	8.3229	.0025	
113	29	68	2	1	2.34	———*	8.5707		
127	31	64	4	1	2.06	8.3712	8.3721	.0009	
132	33	62	4	1	1.88	8.3305	8.3270		.0035
133	33	64	2	1	1.94	8.5564	8.5558		.0006
134	32	65	2	1	2.03	8.5749	8.5713		.0036
137	31.7	63.3	4	1	2.00	8.3147	8.3242	.0095	
138	33	60	6	1	1.82	8.0793	8.0759		.0034
140	38.2	57.8	3	1	1.51	8.4969	8.4568		.0400

*No unannealed specimen available.
**Composition by analysis (Michener's thesis referred to above).

TABLE II

Showing the Corrosion Losses of the Sand-Cast Cu-Ni-Al-Mn Alloys before and after Annealing*

No.	Loss in Mg. per Sq. Cm. in Hot 4 N HNO_3 Before Annealing	After Annealing	Increase in Corrosion	Decrease in Corrosion
104	71.4	49.1		22.3
105	26.8	11.7		15.1
106	52.6	13.2		39.4
108	117.5	48.3		69.2
109	24.3	18.0		6.3
113	63.8	57.2		6.6
127	112.0	362.6	250.6	
132	36.4	35.7		.7
133	231.0	326.2	95.2	
134	328.0	388.6	60.0	
137	100.0	146.7	46.7	
138	164.0	11.8		152.2
140	320.0	319.2		.8

*Numbers omitted were either duplicates or contained metals other than manganese

corrosion factor which was easily within the unavoidable experimental variation for this test. Two other specimens, numbers 133 and 134, showed large increases in corrosion and only small decreases in density while all others showed a decrease in density and a decrease in corrosion, altho the improvement for number 132 and for 140 was not significant. If one were inclined to generalize it might be said that, for the most part, an increase in density was accompanied by loss in corrosion resisting properties and vice versa. This is not believed to be strictly accurate however as will be pointed out below under the discussion of results.

Table III shows the corrosion factors for certain of the alloys which were

TABLE III

Showing the Corrosion Data for Certain Chill-Cast, Sand-Cast and Annealed Cu-Ni-Al-Mn Alloys

No.	Al	Ni/Cu	Loss in Mg. per Sq. Cm. in Hot 4 N Nitric Acid Chill-Cast	Sand-Cast Before Annealing**	Sand-Cast After Annealing
127	4	2.06	249 (No. 145*)	112.0	362.6
132	4	1.88	72 (No. 144*)	36.4	35.7
137	4	2.00	20 (No. 142*)	100.0	146.7
138	6	1.82	58 (No. 146*)	164.0	11.8

*Number assigned to chill-cast alloys.
**From a thesis written by L. J. Wood at the University of Illinois.

cast both in chill molds and in sand molds and also the corrosion data for the sand-cast alloys after annealing.

Table IV compares the tensile strengths of the chill-cast and sand-cast alloys. Unfortunately it has not yet been possible to secure tensile strength tests for the annealed alloys. Alloy number 132 was the only alloy which

TABLE IV

Showing the Tensile Strengths of Certain Chill-Cast and Sand-Cast Cu-Ni-Al-Mn Alloys

No.	Al	Ni/Cu	Tensile Strength in Lbs. Per Sq. In. Chill-Cast[1]	Sand-Cast**
127	4	2.06	57 700 (No. 145*)	36 250
132	4	1.88	56 200 (No. 144*)	56 925
137	4	2.00	55 900 (No. 142*)	35 475
138	6	1.82	81 000 (No. 146*)	49 550

[1] From a thesis written by L. J. Wood at the University of Illinois.
*Number assigned to chill-cast alloys.
**From the paper by L. J. Wood with S. W. Parr referred to above.

failed to show a large difference in tensile strength between sand-cast and chill-cast bars. This alloy also showed very little difference in corrosion for chill-cast, sand-cast and annealed specimens. Alloy number 137 which had a slightly higher Ni/Cu ratio than number 132 with the same aluminium content,

showed a much greater tensile strength when chill-cast than when sand-cast. The corrosion increased from chill-cast to sand-cast annealed specimen. Number 127 had a higher tensile strength when chill-cast than when sand-cast and its corrosion was less for the sand-cast than for the chill-cast or annealed alloy.

Photomicrographs

Formerly a rather superficial microscopic study indicated that the alloys were essentially solid solution of one kind. The more detailed and careful examination made in this investigation has confirmed the former finding for the most part.

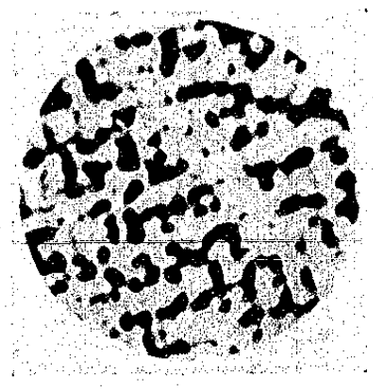


FIG. 1
Ni/Cu 2.09; Al 4; No Mn;
Sand-cast Alloy 103

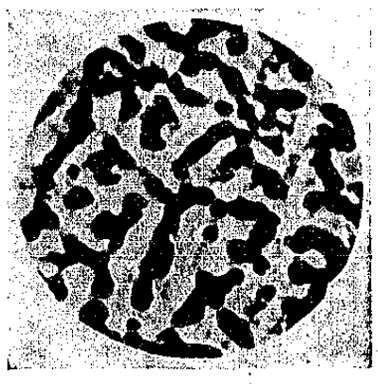


FIG. 2
Ni/Cu 2.06; Al 4; Mn 1;
Sand-cast Alloy 127

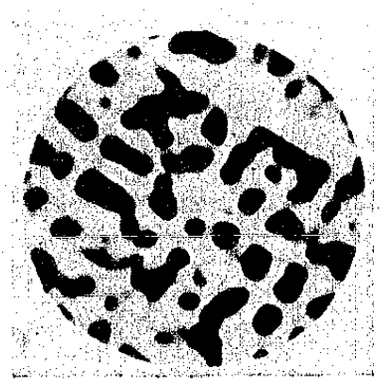


FIG. 3
Composition same as Fig. 2
Alloy 127, annealed

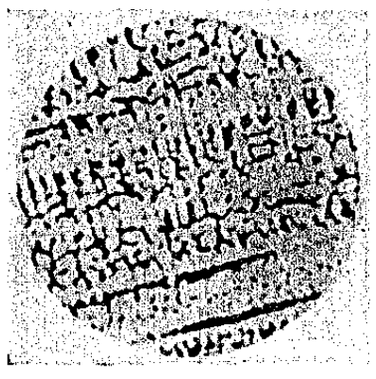


FIG. 4
Composition same as Fig. 2.
Alloy 145, chill-cast

All of these alloys etched with $FeCl_3$ and HCl. Magnification 80 Diameters.

Figs. 1-4 inclusive are quite characteristic of most of the alloys. The familiar dendritic structure, brought out by etching with ferric chloride and hydrochloric acid, shows that they are essentially solid solution alloys of one sort, i.e., the alpha solution. Figs. 5-8 inclusive are photomicrographs of the same alloys photographed without etching or at most with a very slight etch. Alloy 103 contained no manganese. Alloys 127 and 145 were of the same composition as 103 except for one per cent of manganese. Alloy 145 was cast in a steel mold. Alloy 127 was sand-cast and was latter annealed. Fig. 6

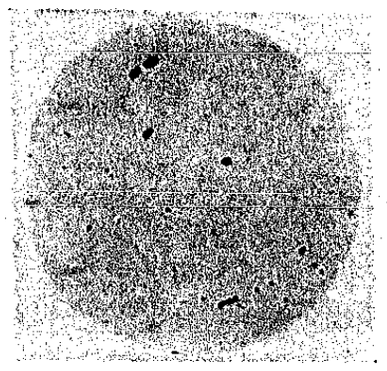


FIG. 5
Ni-Cu 2.09; Al 4; No Mn;
Sand-cast Alloy 103

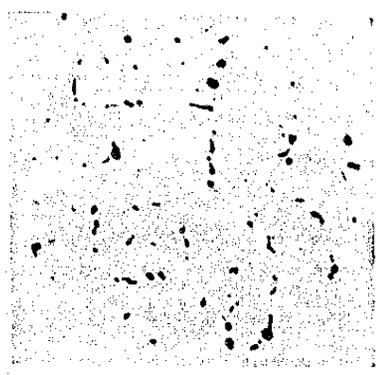


FIG. 6
Ni/Cu 2.06; Al 4; Mn 1;
Sand-cast Alloy 127

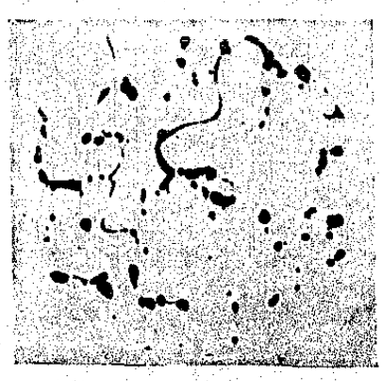


FIG. 7
Composition same as Fig. 6.
Alloy 127, annealed

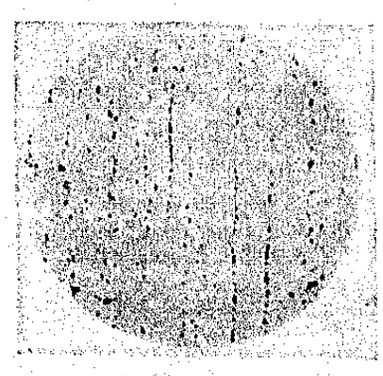


FIG. 8
Composition same as Fig. 6.
Alloy 145, chill cast.

All of these alloys were photographed without etching, magnification 80 diameters.

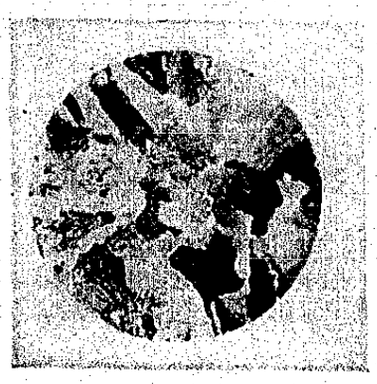


FIG. 9
Ni/Cu 2.09; Al 4; No Mn;
Alloy 103

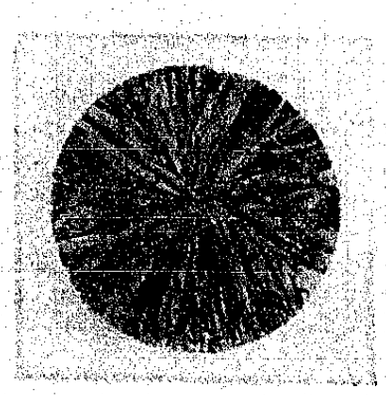


FIG. 10
Ni/Cu 2.06; Al 4; Mn 1;
Alloy 145.

Showing the effect of magnanese on the ternary Cu-Ni-Al.

shows what has been assumed to be small amounts of an alpha-beta eutectic (See discussion of equilibrium diagram below). The quantity of this constituent is increased in this particular alloy by annealing (Fig. 7) and decreased by chill-casting (Fig. 8). Little or none of the secondary constituent is to be seen in alloy 103 which contained no manganese (Fig. 5). This is characteristic of the effect of the manganese observed for most of the alloys but in most cases the annealing has the opposite effect from that noted here.

Fig. 9 shows the structure of alloy 103 (without manganese) deeply etched at two diameters magnification and Fig. 10 shows the same thing for alloy 145 (with manganese).

Equilibrium Diagram

The binary equilibrium diagram of aluminium and copper seems to have been quite well established by the work of Carpenter, Stockdale, and others. Aluminium dissolves in copper up to 10% aluminium, forming an alpha solid solution. The solubility is about 9% aluminium at lower temperatures. Aluminium also dissolves in nickel up to 15% aluminium, forming an alpha solid solution according to the work of Gwyer[1]. The work of Guertler and Tammann on the copper-nickel binary is well known and needs no further comment.

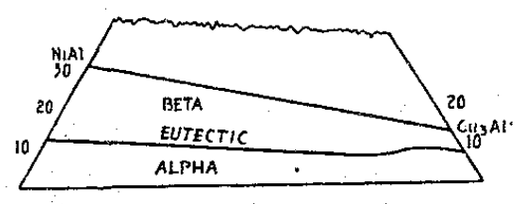


FIG. 11
Showing composition of α-β eutectic in the ternary Cu-Ni-Al at temperatures just below the solidus according to Austin and Murphy.

The ternary Ni-Cu-Mn has been examined by N. Parravano[2] who reports complete miscibility in the solid state. The ternary Ni-Cu-Al has been examined in considerable detail by Austin and Murphy[3]. At temperatures just below the solidus, an alpha solid solution is formed in high copper alloys up to 8% aluminium and up to 12% aluminium in nickel alloys as is represented in Fig. 11, which is a copy of a diagram by Austin and Murphy. At this upper limit of aluminium solubility a eutectic is formed between alpha and beta solid solutions. The beta constituent is said to be a solid solution of the two compounds NiAl and Cu_3Al.

In annealed alloys L. Guillet[4] found that the aluminium instead of being more soluble in high nickel alloys was less. Aluminium dissolved in high copper alloys with a little nickel up to 10%, while in an alloy of 83% copper only 5% aluminium dissolved and in alloys of 60% copper, aluminium did not dissolve until 10% aluminium was reached. According to the work of Austin and Murphy this would be when the beta solution was formed.

[1] Z. anorg. Chem., **57**, 113 (1908).
[2] Gazz., **42** II, 385 (1912).
[3] J. Inst. Met., **29**, 327. (1923)
[4] Compt. rend., **158**, 704. (1914)

Discussion

Our alloys were low in aluminium (2% to 6%) and the copper was much lower than the alloys described by Guillet. According to Guillet, in annealed alloys of this composition no aluminium should be retained in solution. According to Austin and Murphy at temperatures just below the solidus the aluminium should be entirely soluble. The Cu-Ni-Al alloys prepared in this work, of which number 103 is representative, were cast in sand molds and allowed to cool to about 800°C before quenching. The temperature then is intermediate between that of Austin and Murphy and that of Guillet. Little or no evidence for the existence of the alpha-beta constituent in alloy number 103 (Ni/Cu 2.09, Al 4) could be obtained (Fig. 5) but in another alloy of a slightly higher Ni-Cu ratio (Ni/Cu 2.38, Al 2) considerable alpha-beta constituent could be seen. The solubility of the aluminium appears to decrease with decreasing temperature. The solubility also appears to decrease with rising Ni-Cu ratio.

Effect of Manganese

The general effect of the manganese was to precipitate out a second constituent as is illustrated by Figs. 5 and 6. This second constituent has been assumed to be an alpha-beta eutectic. All of the alloys listed in Table I were examined under the microscope but most of them were not photographed. The alpha-beta constituent was identified with great difficulty since it always occurred at the corners of the dendritic structure developed upon etching which appeared dark. Relief polishing brought out the eutectic which was harder but also rounded out the softer copper-rich crystals. When examined by oblique illumination instead of direct illumination, the eutectic appeared as a mountain peak or ridge depending upon the amount present. At best the microscopic examination was not entirely satisfactory and the author is assembling an X-ray equipment for further study.

However it seems fairly certain that high corrosion resistance and high tensile strength depend upon the formation of a homogenous solid solution. Since the manganese, with a high aluminium content causes precipitation of the eutectic the Ni-Cu ratio must be lowered just enough to allow solution to occur but not enough to lower the aluminium effect.

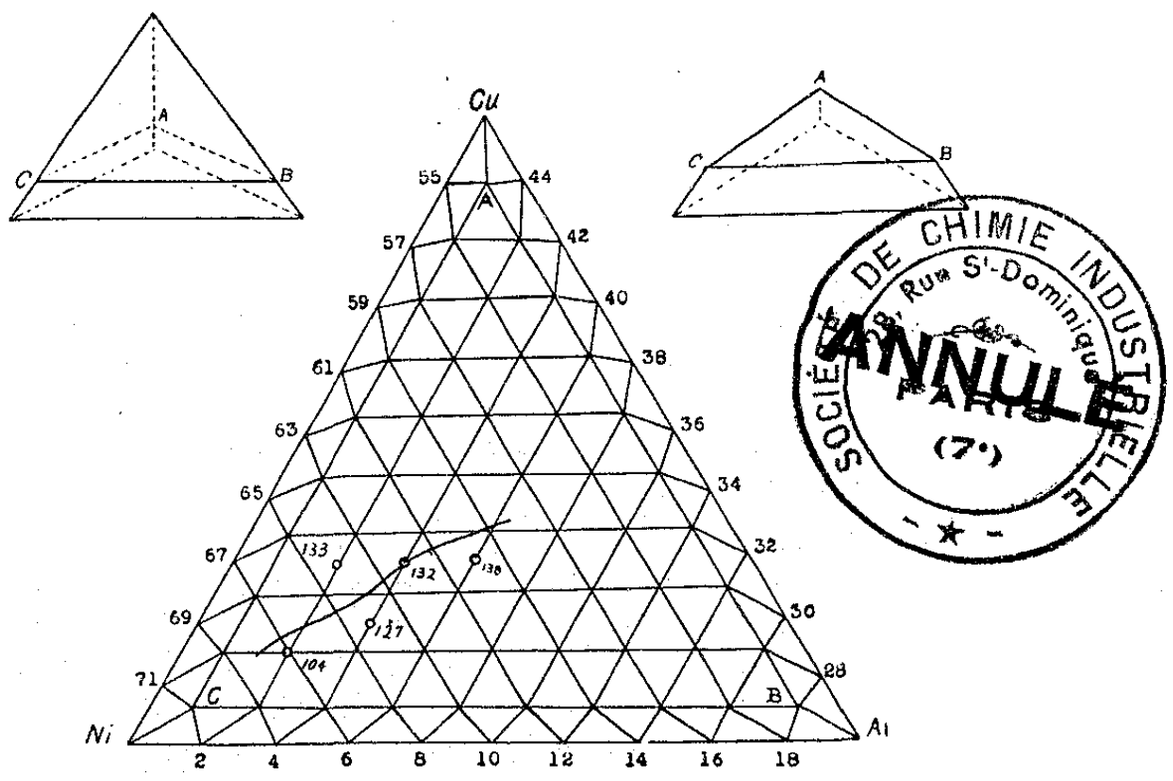
The dark spots of the dendritic structure (Figs. 1-4) are undoubtedly the low-melting parts of the cored crystals and hence are high in aluminium. Apparently the aluminium gets high enough to form the eutectic described by Austin and Murphy. Annealing then would tend to dissolve the eutectic and by experiment this was accompanied by a decrease in density and a decrease in corrosion (Tables I, II). If however the Ni/Cu ratio is too high to dissolve the eutectic upon annealing, some of the solid solution formed at higher temperatures, would be expected to have a tendency to be resolved into the eutectic. Judging from the results obtained when the eutectic went into solution on annealing the density would be expected to increase in this case as would also the corrosion. In the case of alloys 127 and 137 (Figs. 6 and 7) these predictions were realized. If on the other hand the Ni/Cu ratio be-

comes much lower than is necessary for complete solution the corrosion is increased on account of the high copper (alloys 133 and 134).

The annealing effect, when only relief of strains and change in crystal sizes are involved, seems to be that of decreasing the density. In the case of alloys with the proper Ni/Cu ratio corrosion is also decreased (alloy 132). In the case of some of the alloys this same effect was intensified by the dissolving of the eutectic an example of which was alloy 138. In a few cases however the two effects seemed to oppose each other (alloy 127). There was practically no density change while there were important changes in structure and corrosion.

"Maximum Alloys"

What might be defined as "a maximum alloy" for this part of the system will be one whose composition is such that the Ni/Cu ratio and the aluminium



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FIG. 12

Showing relation of Ni-Cu ratio to aluminium content for "maximum alloys."

content are so related as to hold the manganese in alpha solid solution in the most stable form. The proper Ni/Cu ratio will of course vary with the aluminium content, as will also the absolute values of its properties so that it might be possible to plot a curve containing a whole series of "maximum alloys." In this curve there would be "the maximum alloy."

Of all the alloys prepared, number 132 possibly represents nearest "the maximum alloy" of this part of the system Cu-Ni-Al-Mn. The density decreased only slightly upon annealing and the corrosion was practically the same in chill-cast, sand-cast and annealed alloy. Also its tensile strength

was practically the same for the chill-cast as for the sand-cast metal (Table IV). Only a small amount of the alpha-beta constituent could be seen and was about the same in all three conditions, that is, annealing had little effect, not even in decreasing corrosion which might be expected from the removal of strains. There probably were no internal strains to remove. The Ni/Cu ratio was 1.88 and the aluminium percentage 4. The correct Ni/Cu ratio for a 2 per cent aluminium alloy seems to be about 2.23 and for a 6 per cent alloy about 1.82 or lower. The correct Ni/Cu ratio appears to fall with increasing aluminium content as is shown approximately by the curve in Fig. 12. Alloys below the curve in general showed an increasing amount of the eutectic upon annealing. Those above the curve were too high in copper.

Crystal Lattice Types

Copper, nickel and aluminium are known to crystallize in the face-centered cubical lattice. The fundamental cube edge of copper is reported to be 3.6 A. u., nickel 3.54 A. u. and aluminium 4.05 A. u. The lattice type of manganese is yet uncertain but the X-ray spectrum obtained from this element is usually quite complex. It has been suggested by E. C. Bain[1] that this complex spectrum might be due to impurities and that very pure manganese might produce the body-centered pattern. It is not difficult to see why a small increase in the per cent of aluminium has such a large influence on the Ni/Cu ratio when it is considered that the atomic per cent is roughly double the per cent by weight. Also the large difference between the lattice dimensions of the aluminium and that of the copper and nickel would allow the aluminium to exert a large influence.

The manganese lattice type is different from the other three. In the case of german silver the zinc crystallizes in a close-packed hexagonal lattice while the nickel and copper have the same lattice type. In the case of chromium-copper-nickel acid-resisting alloys the chromium crystallizes in the body-centered lattice while the nickel and copper have the face-centered lattice type. Borchers' non-corrosive alloy contains chromium, cobalt and nickel. Again the chromium has a body-centered lattice while the cobalt and nickel have face-centered lattices. In a list of non-corrosive alloys prepared by Campbell[2] approximately fifty non-corrosive alloys are mentioned and in no case in a ternary alloy described in which all three constituents possess the same lattice type. Copper, nickel and aluminium all posses the same type of lattice. It has been shown in this work that the presence of manganese in copper-nickel-aluminium alloys causes a great improvement in the properties of the alloys. The manganese crystallizes in a different lattice type from copper, nickel or aluminium.

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[1] Chem. Met. Eng., **28**, 21 (1923).

[2] Proc. Am. Soc. Testing Mat., **22**, Part I (1922).

Summary

Data and photomicrographs have been submitted which lend support to the following statements.

1. Alloys of the Cu-Ni-Al system having a Ni-Cu ratio of approximately 2 and an aluminium content of 2 to 6 per cent have been shown to form essentially an alpha solid solution when sand-cast and quenched from just below red heat.

2. One per cent of manganese added to the alloys tends to cause a separation of a second constituent.

3. This second constituent behaves as a alpha-beta eutectic would be expected to behave.

4. Chill-casting tends to minimize the amount of alpha-beta constituent in the alloy.

5. Annealing generally causes a decrease in the alpha-beta constituent and also a decrease in density and in corrosion.

6. When annealing causes an increase in the alpha-beta constituent, the density and corrosion of the alloy also increases.

7. The maximum combination of valuable properties of the alloys decrease with increasing amounts of the alpha-beta constituent.

8. The relation between the Ni-Cu ratio and aluminium content is very important. To produce valuable alloys this ratio must be just low enough to form an essentially homogeneous alpha solution.

248-163

THE PHYSICAL CHEMISTRY OF COLOR LAKE FORMATION. II. ADSORPTION OF TYPICAL DYES BY BASIC MORDANTS

BY HARRY B. WEISER AND EVERETT E. PORTER

In the first communication under the above title[1] a study was made of the influence of the hydrogen ion concentration on the adsorption of an inorganic anion, sulfate, and an organic anion, oxalate, both separately and simultaneously by the hydrous oxides of iron, chromium, and aluminum, which are the most common basic mordants or lake bases. Some preliminary observations were also made on the effect of calcium ion on the adsorption of anions by the hydrous oxides at constant hydrogen ion concentration. The results of these observations which have been summarized at the conclusion of the paper, paved the way for a study of the mechanism of lake formation and the effect of the hydrogen ion concentration as well as the presence of other ions on the lake formation process. The results of this study will be reported in this and subsequent communications.

Experimental Procedures

The general methods of procedure were the same as previously described in detail: A definite amount of dye solution was mixed with a definite quantity of a highly purified hydrous oxide sol which was precipitated. The same sols were used as in the earlier experiments. The adsorption was determined from the difference in the concentration of the solution before and after mixing with the sol. The hydrogen ion concentration was measured by means of the hydrogen electrode before and after precipitation. The variations in the hydrogen ion concentrations were accomplished by adding suitable amounts of alkali hydroxide or hydrochloric acid. The effect of the presence of the alkali cations and of the chloride ion was found to be negligible in comparison with the very much more strongly adsorbed hydrogen, hydroxyl, and dye ions.

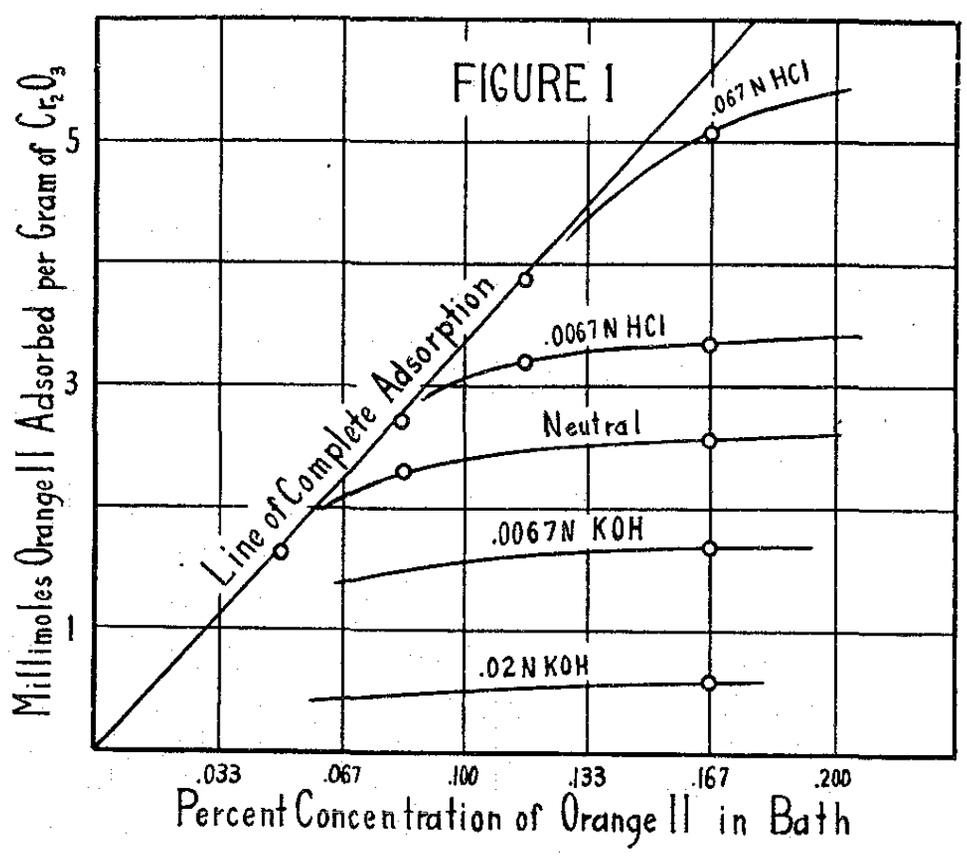
Analysis of Dyes. Considerable attention was given to the accurate quantitative estimation of the dyes whose adsorption was measured. It was recognized at the outset that colorimetric methods would be unsatisfactory both because of errors inherent in colorimetric work and because of the marked influence on the colors of the dyes of minute changes in hydrogen ion concentration. Knecht's method[2] of titrating the dye with titanous chloride was found to be quite satisfactory for the determination of varing concentrations of methylene blue, orange II, and metanil yellow, the dyes used in this investigation. Methylene blue serves as its own indicator giving a reversible change at the end point which is as clean cut as the starch-iodine indicator. Orange II and metanil yellow require an excess of titanous chloride for quanti-

[1] J. Phys. Chem., **31**, 1383 (1927).
[2] Ber., **36**, 1552 (1903); **40**, 3819 (1907).

tative reduction, necessitating back-titration with ferric salt and the use of an outside indicator. Special precautions are necessary to prevent the oxygen of the air from coming in contact with the reducing solution.

Adsorption of Orange II.

Adsorption by Hydrous Chromic Oxide at Constant Initial pH Values. Determinations of the adsorption of orange II anion were readily accomplished at all pH values but the determination of the pH in an orange II solution was found to be unsatisfactory unless the solution is slightly acid, or the concentration of the dye is low, since the dye undergoes reduction at the electrode.



To determine the effect of the concentration of the dye on the amount adsorbed at constant initial pH value, three series of experiments were carried out using hydrous chromic oxide as adsorbent: 1, without the addition of acid; 2, from an initial HCl concentration of .0067 N; 3, from an initial HCl concentration of .067 N. The results are recorded in Table I and plotted in Fig. 1. The results show that a little acid, 0.0067 N, produces a marked effect on the adsorption capacity of the nearly neutral sol, while a larger amount does not increase the adsorption proportionally. Since in the most acid mixtures, the isotherm flattens out before the concentration of dye is as great as 0.167%, it was concluded that this quantity is sufficient to bring the adsorption to the flat of the isotherm in all similar mixtures.

Adsorption by Hydrous Chromic Oxide and by Alumina at varying pH Values. The results of these observations are given in Table II and Table III and

TABLE I

Adsorption of Orange II by Hydrous Chromic Oxide from Different Concentrations of the Dye and of Acid

50 cc of sol containing 0.125 grams of Cr_2O_3 was mixed with the acid and the dye and water to make a volume of 150 cc.

Initial % concentration of orange II in mixture	Series No. 1 No acid Adsorption Millimoles per g Cr_2O_3	Series No. 2 0.0067 N HCl Adsorption Millimoles per g Cr_2O_3	Series No. 3 0.067 N HCl Adsorption Millimoles per g Cr_2O_3
0.050	1.62	not precipitated	not precipitated
0.083	2.29	2.75	not precipitated
0.117	———	3.22	3.86
0.167	2.56	3.32	5.10

TABLE II

Adsorption of Orange II by Hydrous Chromic Oxide at varying pH Values

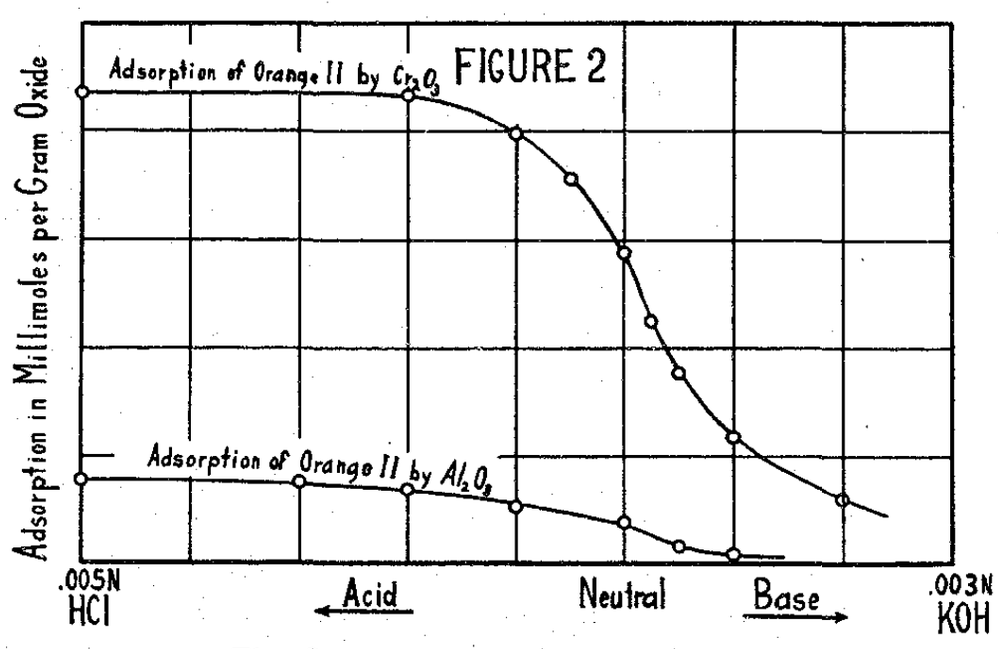
Cc of solutions mixed with 50 cc of sol containing 0.125 gram of Cr_2O_3 in a total of 150 cc			Adsorption value in millimoles of Orange II per gram of Cr_2O_3	pH value of mixture
0.037 N HCl	0.0358 N KOH	0.5% dye		
27.0	0.0	50	4.37	2.65
10.8	0.0	50	4.32	3.17
5.4	0.0	50	3.97	7.55
2.7	0.0	50	3.58	
0.0	0.0	50	2.87	8.316
0.0	1.12	50	2.24	8.532
0.0	2.79	50	1.78	
0.0	5.58	50	1.19	
0.0	11.16	50	0.51	

TABLE III

Adsorption of Orange II by Hydrous Alumina at varying pH Values

Cc of solution mixed with 5 cc of sol containing 0.0085 gram of Al_2O_3 in a total of 20 cc			Adsorption value in millimoles of Orange II per gram of Al_2O_3
0.037 N HCl	0.0358 N KHO	0.5% dye	
2.7	0.0	5	0.76
1.62	0.0	5	0.76
1.08	0.0	5	0.67
0.54	0.0	5	0.52
0.0	0.0	5	0.40
0.0	0.23	5	0.13
0.0	0.45	5	0.07

plotted in Fig. 2. The pH values up to those in the neutral solution are accurate while above 7 the accuracy is questionable since an alkaline solution of the dye undergoes reduction at the hydrogen electrode. It will be noted that the adsorption curve is strikingly similar to those obtained with oxalate and sulfate. The orange II is somewhat less strongly adsorbed than either oxalate or sulfate. This might be expected since orange II acts only as the salt of a monobasic acid under the conditions of the experiment. However, the adsorption is quite strong, in accord with the usual rule that complex organic ions are adsorbed more strongly than simple inorganic ions of the same valence.



The Question of Compound Formation

In view of the fact that the curves representing the amount of orange II taken up by hydrous chromic oxide are continuous both when the initial concentration is left constant while the hydrogen ion concentration is varied and when the initial hydrogen ion concentration is kept constant and the dye content varied, there seems little reason to doubt but that the lake formation process is a typical adsorption phenomenon, the composition of the lake depending on the physical character of the hydrous oxide, the concentration of the dye, and the hydrogen ion concentration of the bath. From similar investigations on the dry gel, Marker and Gordon[1] arrive at the contrary conclusion, that the lake formation process is essentially one of compound formaation between the hydrous oxide and the dye at a suitable hydrogen ion concentration. Typical data furnished by Marker and Gordon are given in Table IV and plotted in Fig. 3 for the taking up of orange II by the hydrous oxides of iron and aluminum. Two grams of dry gel were digested for one hour at 100°C with 0.5 percent dye solution and the change in concentration noted. The hydrogen ion concentration was increased by the addition of sulfuric acid.

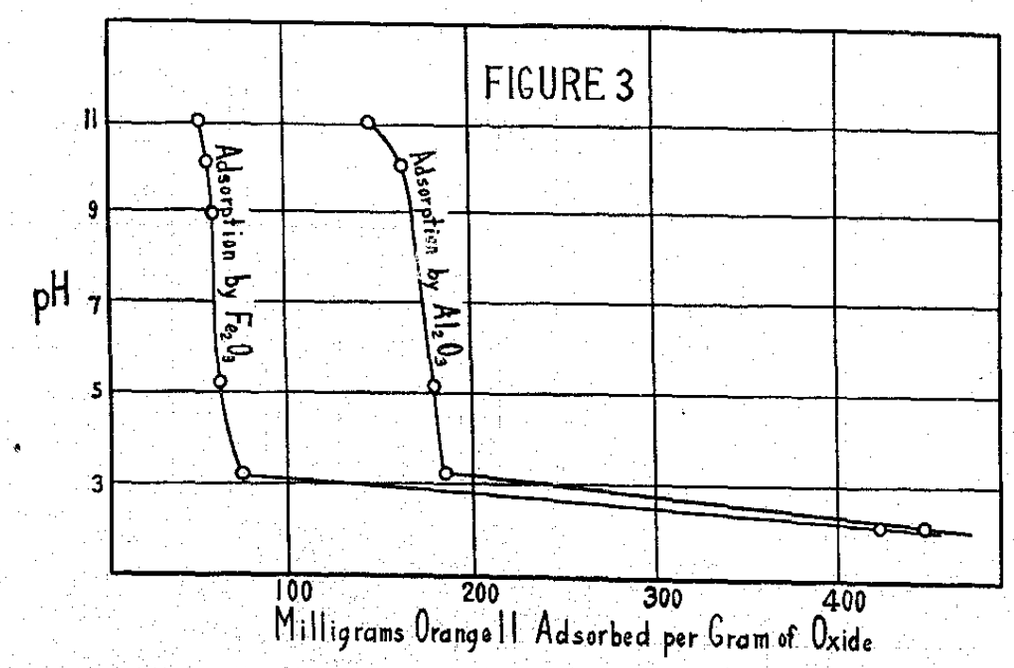
[1] J. Ind. Eng. Chem., **16**, 1185 (1924).

TABLE IV[1]

Adsorption of Orange II by Soil Colloids

Ferric Oxide Hydrogel		Alumina Hydrogel	
pH	Adsorption per gram of gel	pH	Adsorption per gram of gel
2.30	429.0	2.30	452
3.20	78.0	3.20	196
5.37	70.0	5.37	179
10.14	52.0	10.14	162
11.02	50.0	11.02	136

[1] Marker and Gordon: J. Ind. Eng. Chem., 16, 1186 (1924).



It will be seen from Fig. 3 that Marker and Gordon obtained very little adsorption until a pH value around 3.0 was reached when the amount carried down increased enormously. The breaks in the curves were regarded as unmistakable evidence of compound formation which was believed to take place in accord with a reaction which may be represented thus:

$$Na\,X \rightleftarrows H\,X \overset{Fe_2O_3}{\rightleftarrows} Fe\,X_3$$

where X is the anion of the acid dye. Two additional observations were offered as proof that the lakes were compounds: the equilibrium concentration of the dye over the gel in an acid bath was found to be constant and independent of the quantity of dye added; and needle-shaped and threadlike precipitates were obtained with a composition approximating that of the alleged salts. These several facts which were believed by Marker and Gordon to furnish conclusive evidence that the lakes are compounds, will be considered separately.

The Form of the pH-adsorption Curve. Referring to Fig. 3 it will be seen that Marker and Gordon's curves showing the amount of orange II taken up

by the hydrous oxides of iron and aluminum undergo a sharp break at a pH value around 3.0. Such a break was not observed in our experiments represented in Fig. 2. Since the two sets of experiments are similar except that Marker and Gordon used a dry gel as adsorbent, the only explanation of the difference which might occur to the casual observer is that Marker and Gordon failed to get adsorption until the acid concentration was sufficiently high to cause peptization of the gel. Actually the marked difference in the behavior is due primarily to the use by Marker and Gordon of sulfuric acid to control the hydrogen ion concentration, whereas we employed hydrochloric acid. Just as we have seen that the adsorption of sulfate is cut down enormously by the presence of an excess of the more strongly adsorbed oxalate, so the adsorption of orange II anion will be cut down by the presence of an excess of sulfate. Moreover, the practical dyer has known for a long time that sulfate ion cuts down the adsorption of acid dyes and we will show in the paper on the alizarin lakes that this effect increases with the concentration of acid in the bath. Accordingly, it is not surprising to find, as Marker and Gordon did, that the adsorption is almost negligible from a pH of 11 to 3.2 in the presence of sulfate ion. But why the sudden increase in the amount thrown down around a pH of 3.0? This is due to the interaction of the acid with orange II to give the corresponding free acid which is only slightly soluble in cold acid solution and hence comes down with the gel. The precipitate is not only not a chemical compound but is not a lake; it is simply an intimate mixture of free orange II acid with hydrous oxide. We did not get a break in the adsorption curve around a pH of 3 since chloride ion does not prevent the adsorption of the dye anion as sulfate does; hence most of the acid dye anion used was adsorbed when the pH value was sufficiently low to give an appreciable concentration of the orange II acid. Moreover, the insoluble acid may tend to form a positive sol in the presence of hydrochloric acid which would not happen in the presence of sulfuric acid.

Precipitation of Needle-shaped Crystals. The mechanism which Marker and Gordon assumed for the formation of compounds by the interaction of orange II with hydrous alumina, is represented by the equation already referred to:

$$\underset{}{NaX} \overset{H^{\cdot}}{\rightleftarrows} HX \overset{Al_2O_3}{\rightleftarrows} AlX_3$$

In order to test this hypothesis they say, "The acid of orange II was prepared and purified and this free acid was shaken with the respective gels until equilibrium was established, when a larger growth of beautiful crystals was obtained in each case. The alumina gel gave needle-shaped crystals, while the ferric oxide gel gave crystals having a twisted threadlike appearance. When subjected to analysis the crystals gave the following percentage composition:

$Al(SO_3C_6H_4N{:}NC_{10}H_6OH)_3$

	Al	Dye Radical	Total
Calculated	2.7%	97.3%	100.0%
Found	2.6%	97.7%	100.3%"

This seems quite conclusive until the results are analyzed. It is not altogether clear just what procedure was followed but apparently, the slightly soluble acid and the insoluble gel were suspended in water and shaken. It is probable that the mixture was digested at 100° since this would be expected to favor the alleged reaction. At any rate, the experiments were repeated both with and without digestion and both in the presence and absence of sulfuric acid. In every case, the presence of crystals was observed in accord with the statements of Marker and Gordon. However, the crystals were not an aluminum salt but were merely the free acid of orange II. A particularly striking crop of crystals was obtained by heating and cooling the mixture. These crystals dissolved in the hot water and reappeared as thread-like masses on cooling. The presence of the gel has some effect on the appearance of the crystals and may prevent supersaturation. There is no doubt whatsoever that the crystals formed in the presence of the gel were the free acid. In the first place, the precipitate is heterogeneous under the microscope, made up of the gel and crystals of the dye acid. In the next place, both the crystals and the gel were insoluble in cold water; but in hot water the crystals dissolve, leaving the gel. The crystals dissolve also on the addition of a little alcohol to the mixture, leaving the gel. Similarly, on shaking with ether the crystals dissolve leaving the gel in the water layer and the ether layer is colored yellow.

If the alleged compound is merely a mixture of gel with the orange II acid crystals, why does the composition correspond to that of a chemical compound? The answer is that it does not unless the two insoluble substances the gel, and the insoluble acid, are mixed in the theoretical ratio and the analysis made for that ratio. We are forced to the conclusion that this unfortunate procedure was followed by Marker and Gordon.

The Constant Equilibrium Concentration. Finally, Marker and Gordon showed that the equilibrium concentration of the dye over the gel in the acid solution was constant and independent of the quantity of dye used. This concentration was 0.04 percent in the case of the alumina and 0.015 percent in the case of the ferric oxide gel. The values were assumed to represent the solubilities of the respective salts in the solution. These observations are misleading and the conclusions incorrect. The equilibrium concentration merely represents the solubility of the free acid under the specific conditions of the experiment. The differences are due to a slight variation in the temperature or in the hydrogen ion concentration, either of which has a pronounced effect.

Since Marker and Gordon assume an appreciable solubility of the alleged salts, a simple consideration of well-established laws of the kinetics of chemical reactions should have suggested the improbability of forming a salt from the much less soluble gel and a weak slightly soluble acid. In order to get the most favorable conditions for the formation of the alleged salt, a solution of orange II was treated with $AlCl_3$. This resulted in the immediate formation of a precipitate which was believed to be due to the simultaneous hydrolysis of the two salts one of a weak slightly soluble acid with a strong base, and the other of a slightly soluble base with a strong acid. If this be true, the precipi-

tate should be a mixture of the hydrous alumina gel and orange II acid. That such is the case is shown conclusively by the following observations. (1) Microscopic examination reveals that the precipitate consists of two independent solid phases. (2) On heating the mixture to boiling, the solution becomes deep red and the characteristic gelatinous precipitate of alumina remains. (3) If the solution is filtered while hot the needle crystal of the free acid separate from the filtrate on cooling. (4) If a little HCl or H_2SO_4 is added to the mixture, complete solution results on heating. If Marker and Gordon's conclusions were correct one should expect this to be the ideal condition for the formation of the aluminum salt. However, prolonged digestion fails to cause it to precipitate: instead, the characteristic free acid crystals separate on cooling leaving the $AlCl_3$ or the $Al_2(SO_4)_3$ in the solution. (5) The addition of a little alcohol to the mixture causes the solution of the free acid and leaves the alumina which is rendered almost colorless by a few washings with dilute alcohol, ammonia, or Na_2SO_4. (6) If the mixture is made slightly alkaline the crystals of acid are dissolved and the alumina is readily washed white.

Adsorption of Metanil Yellow

Like Orange II, metanil yellow gives a precipitate on being acidified with dilute HCl. Marker and Gordon point out that "the metanil yellow adsorption is due to the precipitation of the dye in the acid medium." In the light of our observations with orange II, it seemed probable that the mixture formed by the precipitation of metanil yellow by acid in the presence of a hydrous oxide is an entirely different phenomenon and gives an essentially different product than is obtained when the dye anion is adsorbed from solution to give a color lake.

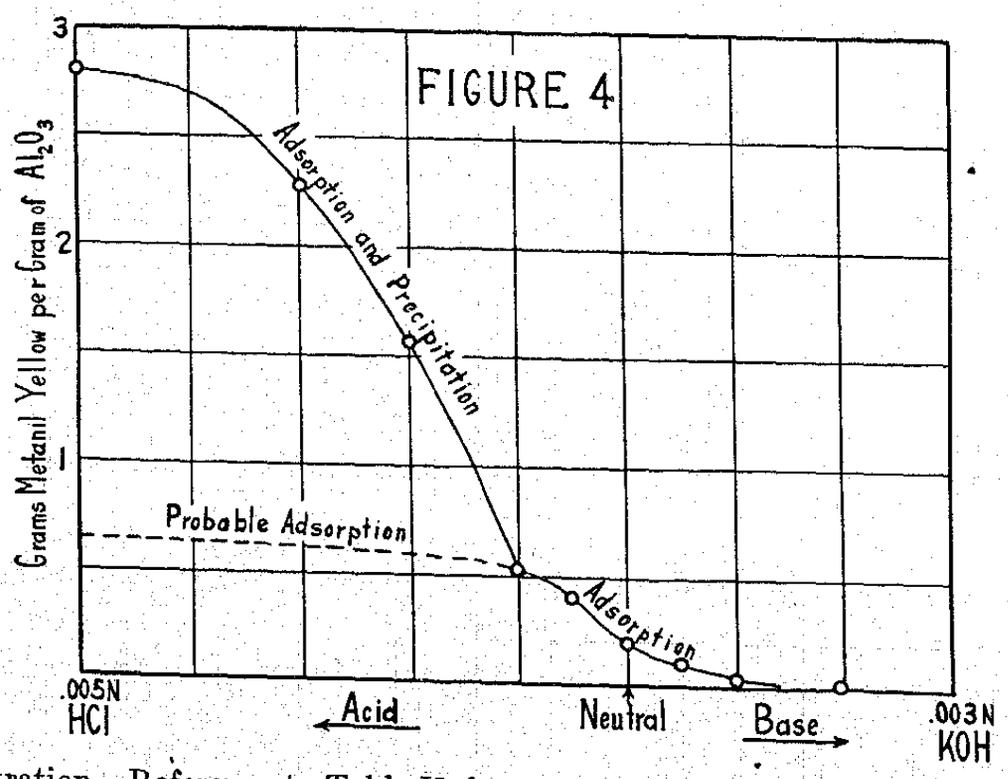
The data on adsorption by hydrous alumina and the precipitation at varying hydrogen ion concentrations are given in Table V and shown graphically in Fig. 4. Similar observations were made with hydrous chromic oxide.

TABLE V

The Behavior of Metanil Yellow and of Alizarin with Hydrous Chromic Oxide and with Hydrous Alumina at varying pH Values

Cc of solution mixed with 5 cc of sol containing 0.000845 grams of Al_2O_3 in a total of 20cc			Apparent adsorption mg per g Al_2O_3	pH values after mixing
0.04 N HCl	0.037 N KOH	2½% Metanil yellow		
2.5	0.0	10	2870	3.160
1.5	0.0	10	2288	5.199
1.0	0.0	10	1571	5.992
0.5	0.0	10	588	7.955
0.25	0.0	10	415	7.970
0.0	0.0	10	187	8.231
0.0	0.27	10	109	9.565
0.0	0.53	10	31	——
0.0	1.07	10	13	——

There is a precipitate of the free acid formed if the HCl concentration of the bath is as great as 0.001 normal. In the more acid solutions the dye bath comes to the same equilibrium concentration regardless of the nature or quantity of the sol present, the concentration being determined by the solubility of the dye under the existing conditions. If the acid mixtures are digested the dye dissolves to give a deep red solution and, in some cases, remains either colloidal or as a supersaturated solution for several days; but in every case, shaking the tube vigorously, causes precipitation and the supernatant liquid returns to the pale yellow as before digestion. This action is similar to that of orange II except that precipitation occurs in a lower hydrogen ion concentration. Reference to Table V shows a normal adsorption curve from the bath when the concentration of the HCl is less thano .001 normal. As the acid is increased above this concentration the precipitation of the dye is proportional to the quantity of acid added until the bath is nearly exhausted. There is doubtless adsorption as well as precipitation from the most acidmixtures.



Adsorption of Methylene Blue

Having studied the adsorption of two typical acid dyes, it seemed advisable to turn to a typical basic dye, methylene blue. Pelet-Jolivet[1] has already shown that methylene blue is adsorbed by the acid mordant, silica, the amount taken up varying continuously with the concentration of the solution. He observed also that the amount of adsorption is determined by the age and the previous history of the mordant. Marker and Gordon did not get a break in the pH-adsorption curve of methylene blue with silica but they got a sharp break with the basic mordants, ferric oxide and alumina, at a pH value

[1] "Die Theorie des Färbeprozesses," 71, 205 (1910).

near 11. It is implied that the lake formed in all cases is a chemical compound; but until someone shows that a very weak base like methylene blue will react with ferric oxide to give a stable salt under special conditions, there is no ground for assuming that the iron-methylene blue lake as ordinarily formed is ever a definite chemical compound. The following experiments bear on this point.

Since methylene blue is a basic dye it is not surprising to find that it is not appreciably adsorbed by the positive sols of the hydrous oxides of the iron group. In Table VI is shown the effect of adding alkali to the hydrous oxide sols of iron and chromium and the corresponding effects on the adsorption of methylene blue. The amount of oxide present was sufficient to make its concentration 0.1 normal. In the adsorption experiments 5 cc of 0.5 percent methylene blue was employed. The total volume in all cases was 20 cc. The adsorption data are accurate at all concentrations but the pH determinations were not satisfactory in the basic solutions in the presence of a considerable quantity of methylene blue.

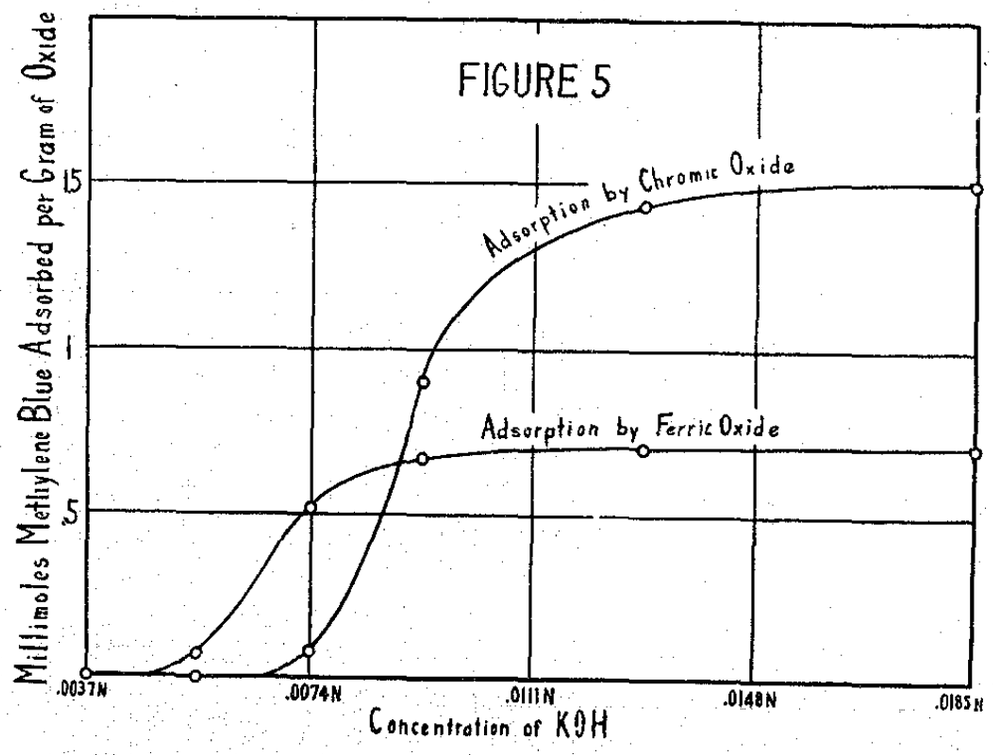
From the data recorded in Table VI and plotted in Fig. 5, it will be seen that the adsorption of methylene blue by both ferric and chromic oxides begins sharply at the concentration of alkali which, in the absence of the dye,

TABLE VI

Adsorption of Methylene Blue from Basic Solutions by Hydrous Oxides

Cc 0.037 N KOH	Effect of KOH alone	Effect of KOH and 5 cc 0.5 percent dye	Methylene Blue Adsorbed	
			Percent of total	Millimoles per gram
	A. Hydrous Chromic Oxide			
0	clear positive sol	not precipitated	0	0
1	not precipitated	not precipitated	0	0
2	precipitation complete	precipitation incomplete	0	0
3	little peptized negative	precipitation incomplete	0	0
4	more peptized	precipitation complete	4.4	0.08
5	nearly all peptized negative	precipitation complete	56.0	0.91
7	all peptized negative	precipitation complete	81.0	1.43
10	all peptized negative	precipitation complete	84.0	1.51
	B. Hydrous Ferric Oxide			
0	clear positive sol	not precipitated	0	0
1	precipitation complete	precipitation incomplete	0	0
2	little peptized negative	precipitation complete	0	0
3	more peptized negative	precipitation complete	4.2	0.07
4	all peptized negative	precipitation complete	30.0	0.52
5	all peptized negative	precipitation complete	38.3	0.67
7	all peptized negative	precipitation complete	40.1	0.70
10	all peptized negative	precipitation complete	41.8	0.72

starts peptization of the hydrous oxides as negative sols. The breaks in Marker and Gordon's curves have this same significance. Above the pH values necessary to start lake formation, the amount of methylene blue adsorbed is a measure of the negative charge introduced by the adsorption of hydroxyl ion; hence it corresponds to the hydroxyl adsorption isotherm. In this connection it will be noted that the maximum adsorption of methylene blue is obtained in the presence of the same concentration of hydroxyl ion which, in the absence of the dye, gives complete peptization of the oxide as a



negative sol. At still higher pH values the adsorption of methylene blue falls off. A similar effect on the adsorption of methylene blue by wool was observed by Briggs and Bull[1] who assigned the effect to increase in the colloidality of the dye in the basic solution. The suppression of the dissociation of the weak base might also be an important factor.

Summary

1. An investigation has been made of the taking up of the acid dyes, orange II and metanil yellow, and the basic dye, methylene blue, by the hydrous oxide mordants, chrome, alumina, and ferric oxide, at varying hydrogen ion concentrations.

2. In every case lake formation consists in the adsorption of the colored ion by the hydrous oxides. There is no indication of the formation of definite chemical compounds between the dye and the mordant at any hydrogen ion concentration.

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[1] J. Phys. Chem., **26**, 845 (1922).

3. The effect of varying the hydrogen ion concentration on adsorption of the dye anion of the acid dyes is comparable throughout to the adsorption of sulfate or oxalate, provided the dye remains soluble.

4. The conclusion of Marker and Gordon that, at low pH values, ferric oxide and alumina react with orange II to form salts has been disproven. The presence of a high concentration of H_2SO_4 in the bath prevents the adsorption of the dye and causes it to be precipitated as the corresponding free acid. The alleged compounds proved to be mixtures of the hydrous oxides and the free orange II acid.

5. A distinction must be made between the precipitation of a dye in the presence of a mordant and the adsorption of the dye by the mordant.

6. Methylene blue is adsorbed by the hydrous oxides only in case the dye bath is sufficiently basic to cause negative peptization of the mordant. The quantity of methylene blue adsorbed from the basic bath is shown to be a measure of the charge on the particles due to the adsorption of hydroxyl ions.

The Rice Institute,
Houston, Texas.

GERMANIUM. XXIII.[1] GERMANIUM MONOSULPHIDE

BY L. M. DENNIS AND S. M. JOSEPH

Germanium monosulphide was first prepared[2] by Clemens Winkler by heating a mixture of germanium disulphide and metallic germanium in a current of carbon dioxide, and also by heating germanium disulphide in a current of hydrogen. In the latter reaction Winkler states that the temperature was carried to "moderate glowing" and he adds that the germanium monosulphide is reduced to metallic germanium at higher temperature.

The present investigation was undertaken to ascertain the optimum conditions for the preparation of germanium monosulphide by heating the disulphide in hydrogen.

Sixty grams of germanium dioxide were converted into germanium disulphide by heating the dioxide with hydrochloric acid through which a current of hydrogen chloride was passed, and precipitating the distillate of germanium tetrachloride with hydrogen sulphide.

The dry germanium disulphide was placed in porcelain boats which were heated in a combustion tube in an electric furnace in a current of dry hydrogen that had been carefully freed from oxygen. Provision was made for testing the escaping gas from time to time for hydrogen sulphide. The temperatures were measured with a thermometer placed within the combustion tube. The changes noted in successive experiments were as follows:

Experiment I:

100° C.—No change.

150° C.—Some moisture from the not thoroughly dry germanium disulphide condensed in the cooler parts of the tube.

200° C.—White germanium disulphide darkened somewhat. First trace of hydrogen sulphide detected in the escaping gas.

250° C.—Powder took on yellowish tinge. Stronger test for hydrogen sulphide.

300° C.—Powder was now distinctly yellow. Strong test for hydrogen sulphide.

350° C.—Powder continued to darken.

375° C.—Reduction continued.

400° C.—Powder was now orange-yellow.

410°–415° C.—Powder turned brown or brownish black. Still strong test for hydrogen sulphide. The temperature was kept constant at this point. Crystals appeared on the side of the tube above the boats, some brown, some black, and some with a bluish luster.

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[1] Contribution from the Department of Chemistry, Cornell University.

[2] Winkler: J. prakt. Chem., **142**, (N. S. 34) 215 (1886.)

Upon completion of the first run, the resulting material was found to be composed of two distinct types of material, one being brownish, and the other black. Examination of the black substance under the microscope showed the presence of large, opaque crystals. These were insoluble in mineral acids.

A second run was made, using more of the germanium disulphide and heating it to a slightly higher temperature.

Experiment II:

415° C.—Material turned to brown and black as before.

420–430° C.—Reduction continued and more of the black, crystalline material was obtained.

In this run the temperature was kept between the limits 410°–430° C. At about 420°, a metallic glint, resembling that of galena, appeared on the walls of the tube.

This second experiment produced a material which showed very little of the brownish substance of the first run, and contained a larger percentage of the black, crystalline product.

A third experiment was carried out at still higher temperatures.

Experiment III:

440° C.—Black, crystalline substance formed in large amounts. Glistening particles formed on the glass above the boat.

450–480° C.—Temperature was maintained within this range. Black glistening particles continued to sublime in increasing quantities on the walls of the tube. These were in the forms of long, needle-like crystals and thin tablets, showing a luster like galena.

It is thus established that the optimum temperature for the reduction of germanium monosulphide lies at about 480° C.

Analysis.—The analysis of the crystalline germanium monosulphide offered difficulties because of the resistance of the substance to the action of solvents. Several different methods were tried with not wholly satisfactory results and finally for the purpose of identifying the compound, the sulphur was determined by combustion in oxygen, the sulphur dioxide being absorbed by a solution of potassium carbonate to which bromine had been added. In the first experiment all of the sample was placed in one boat and when the temperature of the tube reached 800° oxidation took place with considerable violence, and the sulphur dioxide was set free in so large volume as to draw back the solution of potassium carbonate into the combustion tube. This difficulty was avoided by placing small portions of the sample in a series of small porcelain boats in the combustion tube and using a gas combustion furnace, heating one boat at a time. The results of the analysis were as follows: Substance = 0.8733. Wt. of $BaSO_4$ = 1.9084 = 0.2621 S = 30.01 per cent. S.

The calculated percentage of sulphur in GeS is 30.63. It was evident that some of the sulphur still remained in the residue in the boats. This was extracted by a digestion of the boats with their contents in concentrated hydrochloric acid to which 30 per cent. hydrogen peroxide was added from time

to time. From the solution thus obtained an amount of barium sulphate corresponding to 0.00472 gram of sulphur was precipitated. This represents 0.54 per cent. of sulphur in the compound, giving the total sulphur found by analysis 30.55 per cent. which agrees fairly well with the calculated percentage, 30.63.

Properties of Crystalline Germanium Monosulphide.—Very hard, black opaque crystals which are practically insoluble in mineral acids. They are dissolved by fusion with potassium hydroxide and by long digestion with an aqueous solution of potassium hydroxide. When this solution is acidified a reddish brown precipitate of germanous sulphide resulted. Professor C. W. Mason kindly examined the crystalline product under the microscope and reported as follows:—

"Thin tablets, with graphitic luster. Bevelled rectangles with truncated corners. Thinnest flakes and fragments show dark brownish-red to straw by transmitted light, with distinct pleochroism. More opaque than hematite. Probably less than one micron thick to show transmission color. Crystals probably rhombic bi-pyramidal, like tin monosulphide. Faces 010, 1001, 001, 101, 110 present. Terminal angles of tablets 102°."

Summary

The method of preparing germanium monosulphide by heating germanium disulphide in hydrogen as proposed by Winkler was studied, and the conditions for the preparation of crystalline black germanium monosulphide with the avoidance of the separation of metallic germanium were ascertained. The identity of the product was established by analysis, and some of its chemical and physical characteristics are described.

Ithaca, New York.

SOCIÉTÉ DE CHIMIE INDUSTRIELLE
28, Rue S'-Dominique
PARIS
(7e)

THE EFFECT OF MONOMOLECULAR FILMS ON THE EVAPORATION OF ETHER SOLUTIONS

BY IRVING LANGMUIR AND DAVID B. LANGMUIR

This subject first suggested itself to one of the authors several years ago when he was studying the effect of monomolecular films on the surface tension of water. Water, saturated with ethyl ether (5.5 per cent solution) placed in a photographic tray, burns actively when ignited. A globule of oleic acid, however, placed in a corner of the tray, gradually spreads on the surface of the liquid, extinguishing the flame. On further investigation of these phenomena it was found by rough measurements that the rate of evaporation of a saturated ether solution is about nine times as great from an uncovered surface as from one covered by a monomolecular film of oleic acid. The rate of evaporation of pure water was, however, not appreciably changed by the presence of such a film.

One's immediate tendency is to assume that the tightly packed molecules in the oil film form a nearly impermeable membrane which prevents the large ether molecules from escaping, but permits the smaller water molecules to pass. Upon second consideration another hypothesis seems more probable, however.

Careful examination of the surface of an ether-water solution which is partly covered by a film of oleic acid shows that the uncovered parts are in a state of constant motion. This surface twitching can be seen most readily by having the solution in a black tray and observing light reflected from its surface. Traces of talc placed on the surface also show the motions. The twitching increases greatly if one blows upon the solution, and stops if evaporation is prevented by covering the dish with a plate of glass. The presence of a monomolecular oil film completely stops the twitching. Only the uncovered parts of the surface, i.e., those that show the twitching, can be ignited.

These motions of the surface are clearly caused by differences in the surface tension of various parts of the liquid. Variable air currents over the surface of the solution lead to differences in the surface concentration of ether, and produce these variations in the surface tension. The resulting horizontal motions cause vertical currents which bring the concentrated parts of the solution from the bottom of the tray and spread them uniformly over the surface of the solution. The evaporation of ether from the solution is thus aided enormously.

Imagining there were no convection currents in the solution, the rate of evaporation would be very different, however. The ether near the surface would first become exhausted, leaving a layer of water, through which the ether from the lower part of the liquid must diffuse. The evaporation would thus be limited by the rate of diffusion of ether through water—a relatively slow process.

A layer of closely packed molecules on the surface of an ether solution, such as an oil film, would jam together the instant a surface motion began, thus effectively stopping convection currents near the surface, and thus decreasing the rate at which ether could reach the surface.

The experiments described in the present paper were undertaken in order to determine whether the decrease in the rate of evaporation caused by the oil film is, in fact, due to this stopping of convection currents, or is due to an impermeability of the film. A knowledge of the conditions which cause impermeability in a monomolecular film would seem to be of value in understanding many biological problems that involve passage of substances through cell walls.

Hedestrand[1] has attempted to determine the influence of monomolecular films on the rate of evaporation of water in air at atmospheric pressure and 20°C. The dish containing the water was placed in a tube through which a slow current of air was passed. The rates of evaporation (K) ranged from 3.0×10^{-6} to 5.1×10^{-6} gram cm.$^{-2}$ sec.$^{-1}$. The presence of monomolecular films of palmitic or oleic acid did not cause a change in the rate of evaporation greater than one per cent and was therefore not measurable.

Rideal[2] calls attention to the fact that the rate of kinetic interchange between the water surface and the saturated vapor in contact with it, in Hedestrand's experiments, was 0.22 gram cm.$^{-2}$ sec.$^{-1}$, or 43,000 times greater than the observed rate of evaporation.

Thus, even if the true rate of evaporation had been decreased in the ratio 400:1 by the oil film its effect would not have been observed. Rideal measures the rate at which water distills over in vacuum from one leg of an inverted U-tube at 25° or 35°C. into the other leg at 0°C. Rates of evaporation as high as 0.001 gram cm.$^{-2}$ sec.$^{-1}$ are thus obtained, and films of fatty acid decreased this rate very materially. Rideal's data on the rates of evaporation, converted to gram cm.$^{-2}$ sec.$^{-1}$ units, are given in the columns under K in Table I.

We shall find it advantageous to deal with the reciprocals of the rates of evaporation and we shall denote these by R. This quantity measures the

TABLE I

The Effect of Fatty Acid Films on the Evaporation of Water, based on Rideal's Data

Acid	K gram cm^{-2} sec^{-1} 25°C	K 35°C	R cm^2. sec gram^{-1} 25°C	R 35°C	R_F 25°C	R_F 35°C	Ratio of Increase 25°C	Ratio of Increase 35°C
None (pure H_2O)	1040 × 10^{-6}	1470 × 10^{-6}	770.	605.	2.96	1.70	1	1
Stearic	750 "	1160 "	1070.	768.	303.	165.	102.	97
Lauric	600 "	995 "	1340.	895.	573.	292.	193.	172
Oleic	495 "	731 "	1620	1220	853	617.	288.	362.

[1] J. Phys. Chem., **28**, 1245 (1924).
[2] J. Phys. Chem., **29**, 1585 (1925).

resistance to evaporation. In Rideal's experiments there were three resistances in series which were effective in determining the observed rates. There was first a resistance due to the fact that the cold end of the U-tube was at 0°C instead of at the absolute zero. Secondly, there was a frictional resistance opposing the motion of the water vapor through the tube. Thirdly, there was a surface or film resistance which in the case of a contaminated water surface measured the resistance to the passage of the water through the film, but in the case of a pure water surface was determined by the kinetic interchange between the water surface andi ts saturated vapor in accordance with the equation.

$$K = p\ \sqrt{M/(2\pi R'T)}$$
$$= 43.7 \times 10^{-6}\, p\ \sqrt{M/T}\ \text{gram cm}^{-2}\ \text{sec}^{-1} \qquad (1)$$

where R′ is the gas constant, M is the molecular weight (18) and p is the vapor pressures in baryes.

The value of R in Table I includes the second and third of these resistances only, since corrections of 19.6, and 11 per cent respectively have been applied (as was also done by Rideal) to allow for the back pressure of the water vapor in the arm at 0°C.

The resistance R_F for pure water, calculated from Eq. (1) is given in the first row in Table I under R_F. The difference between this and the value of R, viz. 767, and 603 respectively, represents the frictional resistance. Subtracting this constant resistance from the other values in the R column gives the values of R_F for the acid films. The ratios in which the true evaporation resistances have been increased by these films are given in the last two columns. Since these ratios are less than 400:1 we understand why Hedestrand's experiments did not show any increase in resistance.

Experiments on the Evaporation of Ether Solutions

A large quantity of a saturated solution of ether in water was prepared by shaking water with a slight excess of ether. Portions of about 60 grams of this solution were withdrawn by a pipette and placed in shallow glass trays (culture dishes) 9.2 cm. in diameter and 1.2 cm. deep. These trays were weighed at intervals of about 5 minutes to determine the rate of evaporation. An electric fan was used at times to produce a wind of various velocities which were measured by an anemometer placed near the dish.

As the ether evaporates from the solution, the rate of evaporation steadily decreases until finally when the ether is nearly gone the rate approaches that of pure water.

The observed rate of loss of weight is the sum of the rates of evaporation of the ether and of the water. We find that the latter remains constant while the ether concentration gradually decreases. In order to be able to compare the effects produced by various films on the evaporation of the ether from the solution the following method was adopted to reduce each observed rate to that corresponding to a saturated ether solution. This reduced rate expressed in gram cm^{-2} sec^{-1} we shall denote by K_S.

The original water content of the ether solution in the dish was known from the composition of the solution. After evaporation had proceeded to a point where 70 or 80 per cent of the ether content had evaporated, about 8. grams of the solution were withdrawn into a Sprengel pycnometer and from the density the water content was determined.[1] The evaporation was allowed to continue even after practically all the ether had disappeared and the rate of evaporation of the water was thus determined directly. This was found in all cases to agree well with that determined from the pycnometer readings so that we are justified in concluding that the water content decreases linearly with time. This enables us to calculate from the observed weights of the solution the ether content q at the end of each time interval.

It was found by plotting q on semi-logarithmic paper against time that the points lay along straight lines, proving that the rate of evaporation of the ether is approximately proportional to the ether content. If S represents the logarithmic slope defined by $S = \mathrm{d} \ln q/\mathrm{dt}$, then K, the rate of evaporation per unit area at any time is

$$K = Sxz$$

where x is the fraction by weight of ether in the solution and z is the weight of solution per unit area of evaporating surface; i.e. z is proportional to the depth of the solution. For the saturated solution $x_S = 0.055$ grams of ether per gram of solution and we have

$$K_S = 0.055\, Sz \qquad (2)$$

When a small globule of oleic acid is placed upon water or even on a saturated aqueous solution of ether the acid spreads over the surface to form a monomolecular film, while the surplus of acid remains in the globule.

A benzol solution of stearic acid, cetyl alcohol or other such solid substance will spread similarly on pure water, and the surplus of the substance remains as a minute solid island floating on the surface. But these benzol solutions do not spread on water saturated with ether. To produce monomolecular films of these substances on the ether solutions a small amount of water was first put in the glass tray and the film was placed upon it. The ether solution was then introduced under the film by means of a pipette. The small area of the film which was broken by the insertion of the pipette was repaired by covering it with a film of oleic acid formed from a minute globule. This oleic acid film would spread only over those parts of the surface which were not already covered by a film of the first substance added.

The films of oleic acid and cetyl alcohol were liquid but the films of the other substances as used on the ether solutions were solid.

The rates of evaporation K_S of ether from the saturated solutions are given in Table II. The three columns correspond to three wind velocities; v expresses the velocity in cm per sec. It is seen that when no film is present the wind increases the rate of evaporation by a factor of nearly 3, but when the solution is covered by a film the increase averages only about 10 per cent.

[1] The specific gravity of a saturated ether solution at 22° C is 0.9868.

TABLE II

The Effect of Monomolecular Films on the Evaporation of Ether from its Saturated Aqueous Solution

Kind of Film	Temp. °C	$K_S \times 10^5$ K_S in gram cm^{-2} sec.$^{-1}$ $v=0$	$v=61$	$v=152$	$R_S \times 10^{-3}$ R_S in cm.^{2} sec. gram.$^{-1}$ $v=0$	$v=61$	$v=152$	$R_F + R_W$ Average
No Film	22.1	198.	468.	536.	5.0	2.1	1.9	0
Oleic Acid	27.5	28.	31.	31.	36.	32.	32.	30000
Cetyl Palmitate	22.5	31.	30.	33.	32.	33.	30.	29000
Stearic Acid	22.	34.	30.	37.	29.	33.	27.	27000
Cetyl Alcohol	24.5	24.	25.	31.	42.	40.	32.	35000
Myricyl Alcohol	22.	29.	—	—	34.	—	—	29000

The effect of the film is to decrease the rate of evaporation in the ratio 7:1 without wind and 17:1 with a wind of 152. cm. sec^{-1}. All the films tried had roughly the same effect in reducing the evaporation.

The total resistance to evaporation R_S as given in Table II is equal to $1/K_S$. This resistance is clearly made up of three parts.

$$R_A R_S = R_A + R_F + R_W = 1/K_S \qquad (3)$$

Here R_A represents the resistance to diffusion through a layer of relatively quiet air over the solution having a thickness h_A which decreases as the wind increases. This is entirely analogous to the layer of air which determines the heat loss by convection from hot bodies.[1]

The term R_F is the resistance to the passage of the ether through the monomolecular surface film whose thickness is h_F. This resistance may perhaps profitably be looked upon as consisting of two resistances in series; one corresponding to the region occupied by the heads or active ends of the molecules and the other corresponding to the region of the hydrocarbon tails of the adsorbed molecules.

Finally the term R_W is the resistance to diffusion through a layer of quiet water of thickness h_W which underlies the surface film.

The following analysis justifies this procedure of dealing with resistances in series and also enables us to express these resistances in terms of the diffusion coefficient D, the thickness h, and the concentration C in the various layers.

In Fig. 1 the three layers or phases to be considered are represented as before by A, F and W.

Let a substance (ether) pass at the rate K (grams cm^{-2} sec^{-1}) through all three layers in series. The concentrations (in grams cm^{-3}) at the upper and lower boundaries of each phase are denoted by the symbols C_0, C_1, etc., as shown in the figure. If we now stop the diffusion by replacing the boundary

[1] Langmuir: Phys. Rev., 34, 401 (1912); Trans. Am. Electrochem. Soc., 23, 299 (1913).

M by an impermeable membrane, equilibrium will be reached between the phases and the concentrations in the phases become respectively C_A, C_F and C_W. We may now write the equations

$$C_1 - C_0 = h_A K/D_A \qquad C_1/C_2 = C_A/C_F$$
$$C_3 - C_2 = h_F K/D_F \qquad C_3/C_4 = C_F/C_W$$
$$C_5 - C_4 = h_W K/D_W$$

The last two equations assume that a constant partition coefficient exists for each of the boundaries between a pair of phases even when concentration gradients occur within the phases. Because of the high rate of kinetic interchange between the phases this assumption seems justifiable.

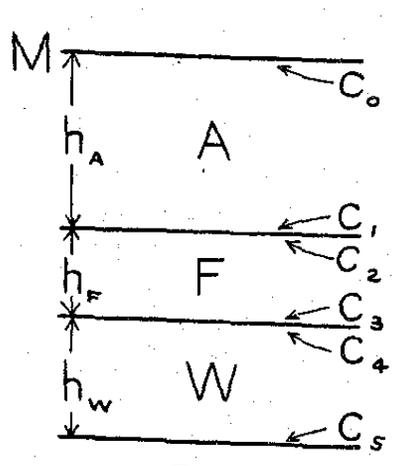


FIG. 1

By eliminating the variables C_1, C_2, C_3 and C_4 by means of four of the equations we obtain a single equation:

$$\frac{1}{K}\left(\frac{C_5}{C_W} - \frac{C_0}{C_A}\right) = \frac{h_A}{C_A D_A} + \frac{h_F}{C_F D_F} + \frac{h_W}{C_W D_W} \qquad (4)$$

In applying this equation to our experimental data on evaporation of ether from saturated solutions, we may put $K = K_S$, $C_0 = 0$, $C_5 = C_W = C_S$ corresponding to the concentration of the saturated solution. Then the factor in parenthesis in Eq. (14) becomes equal to unity and the equation takes the form of Eq. (2). We see that the resistances R_A, R_F and R_W are expressible by the equations

$$R_A = h_A/(C_A D_A)$$
$$R_F = h_F/(C_F D_F) \qquad (5)$$
$$R_W = h_W/(C_W D_W)$$

Let us now examine the values of R_S given in Table II. When there is no contaminating film the resistance R_F vanishes and because of the strong convection currents R_W must be small. The fact that the effect of the wind is to decrease R_S from 5000 to 2000 proves that nearly the whole of this resistance is in the air layer and we may thus identify these values with R_A. Now R_A, although dependent on the wind velocity, will not be materially changed by the presence of an oil film. Subtracting from each of the values of R_S in Table II the value that was obtained for the same wind velocity without the oil film, we obtain the values of $R_F + R_W$.

For example with oleic acid R_S is 36000 with no wind while without the oleic acid $R_S = R_A$ and is 5000. Thus $R_F + R_W$ for this case is 31000. With a wind of 61 cm sec^{-1} this resistance $R_F + R_W$ is 29900 and with a wind of 152 cm sec^{-1} it is 30100. The average value 30300 (rounded off to the nearest thousand) is given in the last column of Table II.

Although the values of R_S decrease with increase of wind velocity, the values of $R_F + R_W$ obtained by subtracting R_A from them, no longer show any distinct dependence on the wind.

Within the probable experimental error, the values of $R_F + R_W$ are the same for all the monomolecular films studied with the possible exception of cetyl alcohol. This fact makes it extremely probable that nearly the whole of this resistance is R_W. This resistance should be independent of the nature of the film provided that this is able to prevent surface currents which induce convection in the underlying liquid. Thus we may estimate the value of R_W for a film-covered surface to be about 30000. Possibly in the case of cetyl alcohol films R_F is about 6000.

To obtain confirmation of the conclusion that R_F is negligible for films of oleic and stearic acids on ether solutions, experiments were conducted with substances that would produce much thinner surface films. It was found that even large quantities of a saturated water solution of caprylic acid added to an ether solution had no appreciable effect on the rate of evaporation, in other words did not interfere with the surface currents.

Butyric acid was then tried with interesting results. Concentrations of this acid from 0.02 up to 0.37 per cent did not have any appreciable effect on the rate of evaporation of ether, but with a concentration of 0.56 per cent the rate fell to 29. $\times 10^{-6}$ (with no wind) which is about the same as with oleic acid. This supports our belief that the stopping of the surface currents rather than the impermeability of the film is responsible for the decrease in the evaporation rate.

We will discuss later the probable cause for the existence of a critical concentration of butyric acid which stops surface currents.

Further striking confirmation of the importance of currents under the film, as affecting R_W was obtained by the following experiment. A saturated solution of ether was covered by an oleic acid film. A match will not ignite this solution, but if a bent glass rod is used to stir the liquid under the film, even without breaking the surface film, the ether will burn readily. If the stirring is stopped the flames gradually go out. Before complete extinction, when only a tiny flame remains, a little stirring immediately sets the whole surface ablaze again.

Effect of Films on the Evaporation of Water

In our experiments, the rate of loss of weight was measured even after the ether had largely evaporated, in order to correct the data for the evaporation of the water. In many cases blank runs were also made to determine the rate of loss of weight of pure water covered by films.

It was found that oleic acid, myricyl alcohol, stearic acid and cetyl palmitate did not appreciably alter the rate of evaporation. This, however, means that the resistance R_F due to these films did not exceed two or three thousand and does not conflict with our conclusion drawn from Rideal's data that these films offer resistances of several hundred units (See Table I).

Films of cetyl alcohol, on the other hand, were found to have a large effect on the rate of evaporation of water, as shown by the data in Table III. The change in resistance produced by the film must be due to the film resistance R_F. The weighted mean of the values of R_F thus found is 65000 cm² sec.

TABLE III

Effect of Cetyl Alcohol Films on the Evaporation of Water

	No wind		Wind of 178. cm sec^{-1}	
	K	R	K	R
No film	2.3×10^{6}	430000	14.7×10^{-6}	68000
With film	1.9×10^{6}	520000	7.8×10^{-6}	128000
Difference	——	90000	——	60000

$gram^{-1}$. Comparing this result with the data in Table I we conclude that the true rate of evaporation ($1/R_F$) of water is cut down in the ratio 20000:1 by the presence of a cetyl alcohol film whereas with oleic acid the ratio is about 300:1.

Repeated experiments have always shown that cetyl alcohol has this marked effect on the evaporation of water. Although cetyl alcohol itself is a solid which melts at about 50°C, the films of this substance on water are liquid even at 4°C. Films of palmitic and stearic acids on pure water are solid but are liquid if a trace of acid is added to the water. The area per molecule is considerably increased by the acid. It was thought that this change might make the film offer a greater resistance to the passage of water.

Careful measurements made with four glass trays in a moderate wind from a fan, interchanging the positions of the trays every five minutes, showed that within the experimental error of about two per cent the rate of evaporation ($K = 14.1 \times 10^{-6}$) of water containing 0.1 per cent of hydrochloric acid and covered with a palmitic acid film was the same as that of pure water. The same was true of water which contained 0.1 per cent of tannic acid and was covered by an oleic acid film, altho in this case the tannic acid gradually forms a solid film on the surface, so thick that it shows brown and even deep blue interference colors by reflected light. Such visible films must be many hundreds of times thicker than monomolecular films of fatty acids.

Factors which determine the Resistances

We have seen from Eq. (5) that the resistances which we have measured are related to the diffusion coefficients D, the equilibrium concentrations C, and the thickness h of the layer or film which causes the resistance.

The diffusion coefficient of ether vapor through air at 20° is 0.089 cm^2 $sec.^{-1}$ according to Winkelmann; at 22° this would be about 0.090. The vapor pressure of a saturated solution is approximately that of pure ether, viz., 480 mm. at 22°C., corresponding to a concentration $C_A = 0.00193$ grams cm^{-3}.

The data for R_A given in Table IV for various wind velocities v are taken from Table II. The third column contains the values of h_A calculated by means of Eq. (5). The last column gives the thickness h_C of the air film that is effective in determining the heat loss by convection from the upper face of a horizontal plane surface of a heated body.[1]

[1] Langmuir: Trans. Am. Electrochem. Soc., **23**, 323 (1913).

TABLE IV

Resistance to Evaporation R_A due to Air Layer over the Solution

temp. = 22°C.; C_A = 0.00193 g. cm^{-3}; D_A = 0.090 cm^2 sec.$^{-1}$

v cm. sec^{-1}	R_A cm^2 sec gram^{-1}	h_A cm.	hC cm.
0	5000	0.86	0.45
61	2100	0.36	0.27
152	1900	0.33	0.19

The agreement as to order of magnitude is sufficiently close to prove that the resistance to evaporation from a pure water surface may be looked upon as a resistance to diffusion through a layer of relatively quiet air. The fact that h_A is greater than h_C is explained by the fact that ether vapor is heavier than air, and thus tends to cling to the surface, while in heat convection the hot air rises.

Thovert,[1] as a result of extensive studies of diffusion of organic substances in solutions, concludes that the diffusion coefficient is always at least approximately given by the equation

$$D = 8 \times 10^{-7}/(\mu\sqrt{M}) \text{ cm}^2 \text{ sec}^{-1} \qquad (6)$$

where M is the molecular weight of the diffusing substance and μ is the coefficient of viscosity (in c. g. s. units) of the solvent through which the diffusion occurs. For the diffusion of ether through water at 22°C. we thus obtain

$$D_W = 9.7 \times 10^{-6} \text{ cm}^2 \text{ sec.}^{-1}$$

Rough experiments have checked the order of magnitude of this result.

We have found that R_W for evaporation from film-covered surfaces is 30,000 (see Table II); C_W for a saturated ether solution is 0.054 g. per cm.[3] Thus Eq. 5 gives h_W = 0.016 cm.

C. W. Rice,[2] by dimensional reasoning, has derived equations for calculating the film thickness in liquids and has proved that these equations agree with the available data on heat transfer by convection in liquids. For the convection currents induced by evaporation of ether from film-covered surfaces the film thickness will be different, but for this case we may in an analogous manner, derive the following equation for the film thickness

$$\frac{h}{d} = k\left[\frac{\mu}{\rho d^{3/2}(\beta g)^{1/2}}\right]^n \left(\frac{D\rho}{\mu}\right)^m \qquad (7)$$

where k is a numerical constant of the order of magnitude of unity which depends only on the type of geometrical form of the surface from which convection occurs (plane, cylinder, sphere, etc.); d is a length which determines the linear dimensions, μ is the viscosity, ρ the density, g the acceleration of gravity, β the fractional difference in density of the solution at opposite faces of the film, D is the diffusion coefficient (of the ether in the water), while n and m are numerical exponents to be determined by experiment.

[1] Ann. Phys., **2**, 369 (1914).

[2] J. Am. Inst. El. Eng., **62**, 1288 (1923).

In the present case we may take d to be the depth of the liquid in the tray. Since the film thickness must be nearly independent of d, we should place n = ⅔. Rice finds m = ¼ for heat convection, and, because of the general similarity in the mechanism of the two kinds of convection we may adopt the same value. Thus, taking d = 1, μ = 0.01, ρ = 1, g = 1000, β = 0.013, $D = 10^{-5}$, n = ⅔ and m = ¼, we find h = 0.0036 k. This dimensional reasoning gives the correct value h_W = 0.016 if we take k = 4.4. From his heat convection data Rice obtained values of k between 2. and 8.7. Thus if we put k = 4.4 in Eq. (7), we should be able to calculate the film thickness and therefore, by (5), the resistance to evaporation in all types of solutions in which the evaporation causes increase in density at the surface.

In this connection it would be of great interest to study the evaporation of aqueous solutions of volatile substances whose density is greater than that of water. In this case the film thickness should become very great and the rate of evaporation should be retarded much more than in the case of ether solutions.

Evaporation Resistance in Monomolecular Films

According to Table I, an oleic acid film, which has a thickness of about 10^{-7} cm., opposes a resistance of about 800 units to the evaporation of water. We see from Eq. (5) that this means that the product $C_F D_F$ must have the value 1.2×10^{-10}. There is no reason for believing that the diffusion coefficient of water molecules among the hydrocarbon tails of the film molecules should be abnormally low. If we calculate D_F by Eq. (6), taking μ = 0.003 (as for pentane), we find $D_F = 6 \times 10^{-5}$, and thus C_F, the concentration of water in the film, would have to be 2×10^{-6} grams per cm.^{3} The viscosity of oleic acid is greater than 0.003, but this is due to the fact that a body moving through the liquid moves transversely to the length of many of the molecules. Water molecules should be able to diffuse through a film of oriented long molecules, in a direction parallel to the length of these, with no greater difficulty than through a film of the same thickness consisting of unoriented shorter molecules.

In the case of cetyl alcohol films where we found R_F = 65000, a similar calculation gives $C_F D_F = 1.5 \times 10^{-12}$ and $C_F = 2.5 \times 10^{-8}$ grams per cm.^{3}. It seems improbable, however, that the solubility of water in these films can really be as small as these figures would require.

The question arises whether the spreading force acting between the molecules can prevent the water molecules from entering the film. If a water molecule enters a liquid film, it must cause the film to expand, by pushing apart its molecules, by an area a_o. Thus it must do the work Fa_o where F is the spreading force (in dynes per cm.). The effect of variation in F on the concentration of water in the film will be given by the Boltzmann equation, which takes the form

$$C = C_o e^{-Fa_o/KT} \qquad (8)$$

where C_o is the concentration when F = 0 and K is the Boltzmann constant 1.37×10^{-16} ergs per degree.

If we take $a_0 = 8 \times 10^{-16}$ cm.^{2} $F = 30$ dynes per cm., T = 300 we find $C = 0.55\ C_0$. Thus the effect of the change in surface tension would only be to decrease the solubility of water in the film to about one half.

It would thus seem that the comparative impermeability of cetyl alcohol and perhaps other films must be due to some rather specific effect produced by heads, or active ends of the molecules, which we have not considered in the theory which led to Equation (5). Probably the electric forces resulting from the electric double layer which undoubtedly exists will be needed to explain the observed impermeability. Similar phenomena probably govern the permeability of cell walls.

Our conclusion that only a moderate decrease in C and therefore in permeability can result in accordance with Eq. (8) from the surface forces, would need modification if the film is solid. With special structure as in the walls of living cells, the permeability may perhaps be altered by changes in the surface forces much more than would be indicated by Eq. (8).

Our experiments have given us no definite evidence that the monomolecular films oppose any direct diffusion resistance to the passage of ether molecules. The great solubility of ether in hydrocarbons suggests that the permeability of these films for ether should be much greater than for water. However, the decrease in solubility caused by the lowering of surface tension according to Eq. (8) will be greater in case of ether because the area occupied by the ether molecule may be several times as great as that of a water molecule.

Some experiments in photographic trays have shown that the maximum area occupied by the film produced from a given small amount of oleic acid on a half-saturated ether solution is about 85 per cent. as great as that occupied by a film containing the same amount of oleic acid on pure water. This indicates that there is no large dilution of the oleic acid film by adsorbed ether molecules.

On the other hand, when no oil film is present the ether molecules in an ether solution are fairly tightly packed in the adsorbed film. Some rough surface tension measurements by the capillary rise method at 22°C have given γ_{obs} in Table V (dynes per cm.)

TABLE V

Surface Tension of Aqueous Ether Solutions

C	γ_{obs}	$\gamma_{cal.}$	A (cm^2)
1 = saturated solution	33.	33.	40.0×10^{-16}
1/2	39.	40.	40.7
1/4	46.	47	42.5
1/8	58	53	46.0
0.022	—	60	78.
0 (water)	73.	73.	∞

The constants A and B of Szyszkowski's equation[1] are found to be B $=0.33$ and A $= 0.022$, the unit for A being the concentration of ether in a saturated solution. Thus γ_{cal} was calculated from

$$\gamma - \gamma_0 = B\gamma_0 \log_{10}(1 - c/A)$$

where $\gamma_0 = 73$. The area a of the surface film, per molecule of ether present in the film, is

$$a = 12.8 \times 10^{-16}\,(C + A)/(BC)\ \text{cm}^2.$$

The values of a from this equation are given in the last column of Table V. It is seen that the film of adsorbed ether molecules is nearly saturated (close packed) even when the solution is only 1/4 as strong as a saturated solution.

The mechanism of the spreading of an oleic acid film on a saturated ether solution may now be better understood. The oleic acid exerts a spreading force on water of about 34. dynes per cm., but the spreading force of ether in a saturated solution is slightly greater, about 40 dynes per cm. ($73-33$, see Table V). However, if any portion of the surface becomes contaminated so that the surface currents are decreased, the evaporation locally lowers the surface concentration and allows the oleic acid to spread. Thus the spreading on the strong solution is a rather slow process.

Similar considerations help to explain the critical concentration of butyric acid that was found necessary to stop the surface currents. According to Szyszkowski's data the surface tension of water containing 0.56 per cent of butyric acid is 62 dynes per cm corresponding to a spreading force of 11. dynes per cm. That butyric acid molecules can accumulate in the surface of an ether solution at all under these conditions is probably only possible when evaporation lowers the surface concentration of the ether. We see that as the strength of the butyric acid increases there results a kind of instability that accounts for the critical concentration observed.

One other phenomenon deserves to be mentioned in this connection. Upon the surface of a saturated ether solution in a photographic tray is placed an amount of oleic acid insufficient to cover the whole surface. The area actually covered can be seen by the absence of surface currents. Now, by a moving barrier the surface area is decreased until the surface is just completely covered by the film. Suppose the area is then 100 cm^2. The area can now be increased to say 120 cm^2 without causing any part of the surface to become uncovered. For example, no part can be ignited. But if the surface is touched with a glass rod, or a little ether vapor is poured from a beaker on to a portion of the surface, an uncovered area of 20 cm^2 suddenly appears and remains on the surface. Clearly the increased concentration of ether vapor over the surface produced in either of these ways causes an increase of ether in the surface film which pushes back the oleic acid.

Summary—Instead of considering the rate of evaporation of a liquid in grams cm^{-2} sec^{-1} there is an advantage in using the reciprocal of this quantity which may be termed the evaporation resistance R in cm.^{2} sec. grams^{-1}.

[1] See Langmuir: J. Am. Chem. Soc., 39, 1890 (1917).

Measurements made by Rideal on the rate of evaporation of water show that the resistance produced by a monomolecular film of oleic acid is 800 units, while in the absence of the film it is about 3 units at 25°C. The writers find that a monomolecular film of cetyl alcohol opposes a resistance of 65000 to the evaporation of water, so that the effect on the evaporation is readily observed in experiments at atmospheric pressure.

The rate of evaporation of ether from its saturated aqueous solutions is cut down to less than one-tenth of its former value by any non-volatile insoluble substance such as oleic acid that can form a monomolecular film upon this solution. It is shown, however, that this is not due to a resistance in the film but results from the effect of the film in stopping surface currents that otherwise stir the underlying liquid because of surface tension variations. The resistance due to an air film over the surface, ranges from 5000 for no wind down to about 1900 with a wind velocity of 1.5 meters per second. With no oil film this is the only resistance that is present. But with an oil film there is in addition a resistance of about 30000 due to an underlying film of water about 0.02 cm. thick through which diffusion must occur.

It is calculated that $R = h/(CD)$ where h is the thickness of any film or layer through which diffusion occurs, D is the diffusion coefficient and C is the concentration of the diffusing substance *when equilibrium* is brought about by stopping the diffusion. This gives for the concentration of water in the cetyl alcohol film $C = 10^{-8}$ grams per cm^3. Some specific factor not taken into account in the theory is probably largely responsible for the high film resistance in this case.

A method is proposed for calculating the resistance due to the underlying liquid layer for any kind of a solution.

Calculation seems to show that the variation of permeability of liquid films with surface tension should be measurable but not very large, but certain solid films, such as those of walls of living cells may show such effects to a much greater degree.

Research Laboratory,
General Electric Co.,
Schenectady, N. Y.

STUDIES IN THE EXPERIMENTAL TECHNIQUE OF PHOTOCHEMISTRY. PART IV

A Critical Examination of Certain Filters for the 365 Mercury Line

BY L. T. M. GRAY

To isolate the strong line in the mercury arc occurring at 365 $\mu\mu$ a number of filters have been suggested, among others by J. Hartmann,[1] Luther and Forbes,[2] Winther,[3] Andrich and LeBlanc,[4] and Bottolph.[5]

Of these the filter of Winther and the Luther and Forbes G1 filter have been favourably noticed by other investigators, and were therefore selected for testing. To these was added the Goerz nickel-oxide glass recommended by Weigert, since no exact data of its transmission were then available.

Experimental

The investigation was carried out by means of a Judd Lewis Photometer in conjunction with a large Hilger quartz Spectrograph and a condensed spark between electrodes of high-speed steel. These electrodes gave a very close spectrum, and one which extended well into the ultra-violet. The plates were spotted by the method suggested by Howe[6] and the mark was always made with a mapping pen on the back, or non-emulsion side of the plate. After the point of equal density had been read off by means of the wave-length scale photographed on the plate, the marks were wiped or scraped off and the spotting repeated. This is necessary since the eye tires very quickly, and so is liable to make an error.

Luther and Forbes G1 Filter.

This filter consists of one solution containing:—

0.0785	grams of	Fuchsine S.	per litre.
0.0164	"	Methylene Blue	"
0.0410	"	P. nitrosodimethylaniline	"

The solution should be 0.78 cm. thick, between glass plates. No cell was available of this thickness, and so a glass plate 6.35 mm thick was used in conjunction with a 1 cm. quartz cell. The Methylene blue used in the first investigation was Casella's DBB, the acid fuchsine, or fuchsine S., came from the British Drug Houses, and the p-nitrosodimethylaniline from Kahlbaum. The colour of the solution was dark brown, and the transmission of this filter is shown in Fig. 1. No compensation or allowance was made for the light absorbed or reflected by the two quartz ends of the cell and the glass plate;

[1] Z. wiss. Phot., **1**, 259 (1903).
[2] J. Am. Chem. Soc., **31**, 770 (1909).
[3] Z. Elektrochemie, **19**, 389 (1913).
[4] Z. wiss. Phot., **15**, 187 (1915).
[5] J. Optical Soc. America, **6**, 1066 (1922).
[6] Phys. Rev., (2) **8**, 680 (1916).

the figures giving the actual percentage of the incident light transmitted through this particular filter. Only two transmission bands appeared, one in the ultra-violet from 330 to 380 with a maximum transmission of about 8% at 365, and the other in the visible above 500.

As it was desired to use this filter for another investigation in the laboratory at a thickness of 2 cm., the same solution was diluted to one fifth of its original strength, and examined at this thickness. The head of the band in the ultra-violet was now about 360, and the transmission at 365 was 30%. The other mercury lines in this region were entirely cut out, while in the visible region transmission started at about 465. The results are also shown in Fig. 1.

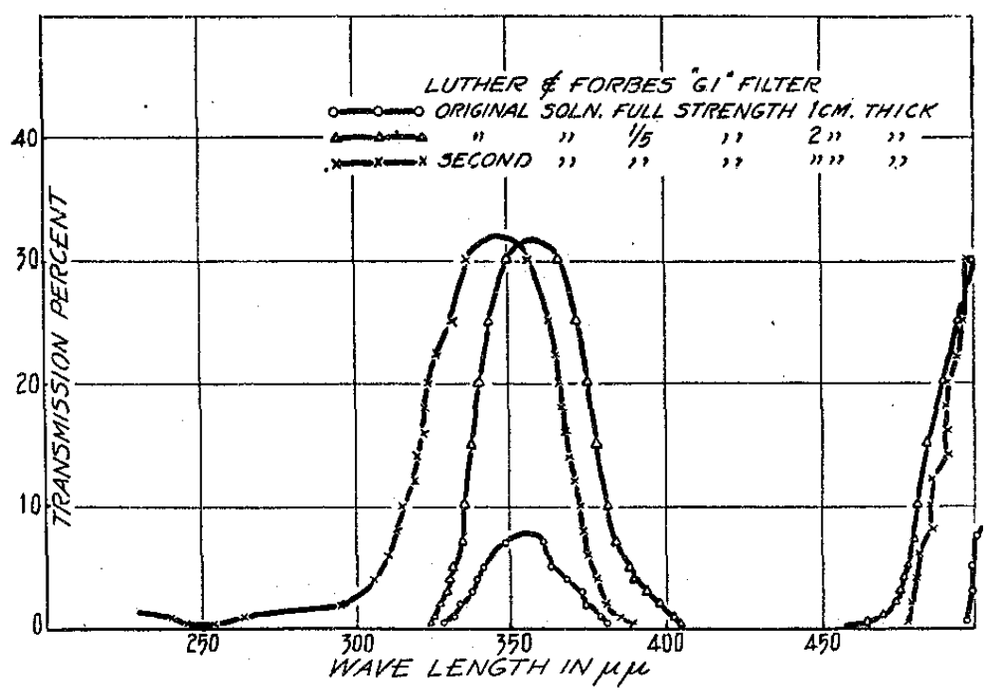


FIG. 1

It was noted that this filter changed colour slightly when allowed to stand in a glass bottle, and thus behaviour was referred to the solution of small amounts of alkali from the glass. In view of this high sensitivity in the visible part of the spectrum to the hydrogen ion concentration, it was thought advisable to test the transmission in the ultra-violet after the addition of known quantities of acid and alkali. A fresh solution was therefore made up from the same samples as before, except that the fuchsine S came from Casella. The transmission was measured in the same way as before, except that the glass plate was omitted so that any movement of the bands could be observed. The transmission was found to be slightly different from that of the previous sample, since the band in the ultraviolet was shifted away from the visible end of the spectrum, the head of the band occurring at about 350. Since the band was of the same height and shape as before, the transmission at line 365 was reduced from 30% to 25%.

Then to different portions of the solution were added one drop each of dilute solutions of hydrochloric acid and sodium hydroxide, the amount of

each drop being measured in a 1 cc pipette, and the volume of the filter solution being 5 cc in each case. The change in colour was marked. The solution was originally olive green, (and thus quite different from the first solution made up, which was definitely brown, with a greenish tinge) which changed to a strong magenta on the addition of the acid, and to grass green on the addition of the alkali. The results are shown on Fig. 2. The effect of the acid is to move all the bands towards the visible end of the spectrum, if we assume that the band at 260 corresponds with the slight band shown by the original solution at about 235. The effect of the alkali is just the reverse.

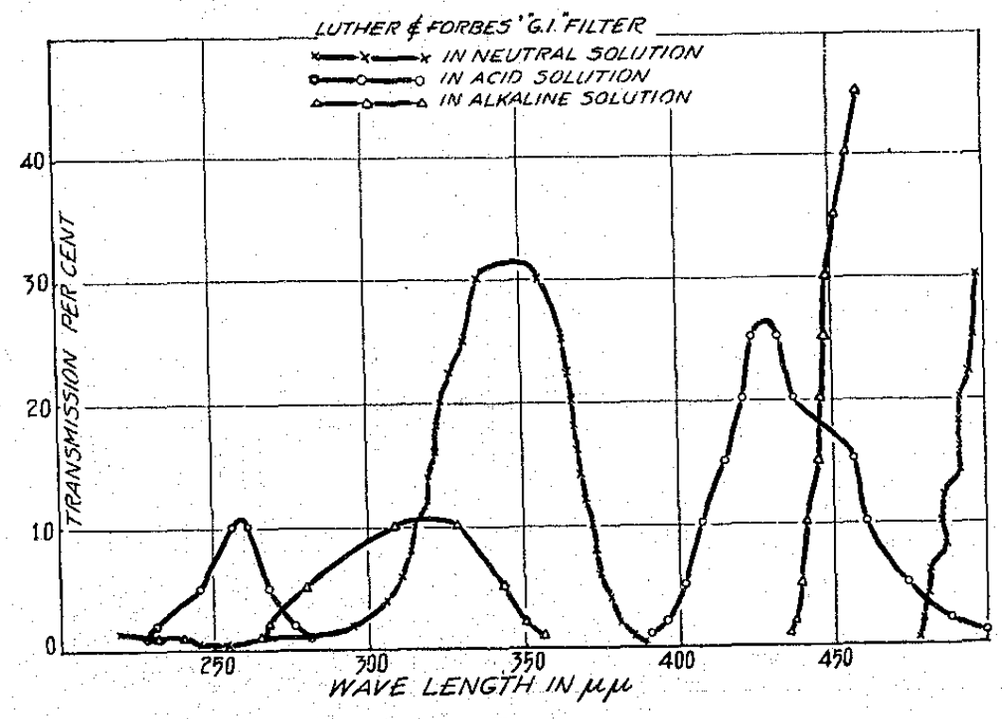


FIG. 2

The acid was calculated to be approximately 0.012 N., and the alkali concentration approximately 0.014 N.

Winther's 365 Filter.

This consists of 1 cm thickness of 0.03% Diamant Fuchsin 1 Grobe Krystalle (obtained from Casella) in water. The transmission was measured in neutral solution, while to other portions acid and alkali were added exactly as to the Luther and Forbes filter. The ends of the cell were of quartz, although it is better to use glass when the filter is employed to isolate line 365. The transmissions of the neutral and acid solutions are shown in Fig. 3. The addition of the acid caused the solution to change in colour from cherry red to crimson, while the addition of the alkali coagulated the dye completely, leaving a colourless solution, which was therefore not measured. In both the solutions measured the transmission for line 365 was about 35%, but the shapes of the two curves were entirely different, the acid solution also passing 30% of line 313 and over 15% of line 406, while the neutral solution made quite an efficient filter.

Goerz Glass.

This glass, which contains nickel oxide in suspension, has recently been brought forward as a filter for the 265 line, and is recommended by Bodenstein. The specimen obtained was 3 mm thick, and certainly seemed to be an efficient filter, transmitting less than 0.5% outside the region 330 to 390. At the point of maximum transmission, however, which coincided with the 365 line, only 6 or 7% was passed. Other workers in this laboratory, using a thermopile and galvanometer, obtained 15% transmission. Their observations were taken through the plate near the edge, whereas those recorded

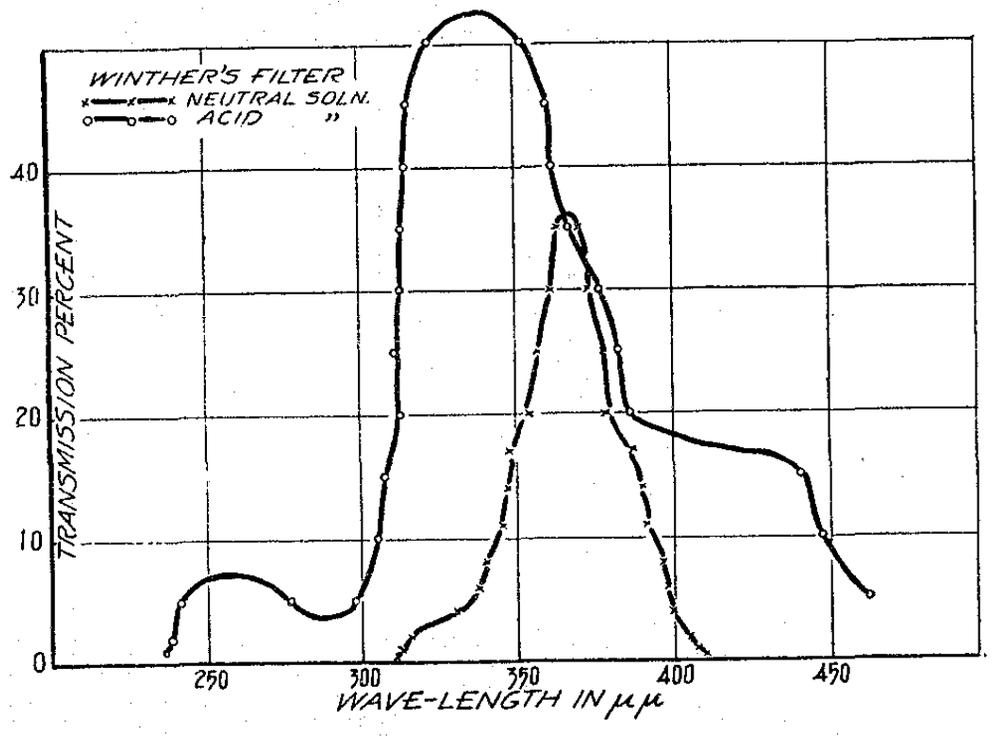


FIG. 3

above were through the middle. On careful inspection the plate was found to be far from homogeneous, a considerable amount of visible light being transmitted near the edges whereas the centre was practically opaque. This is sufficient to account for the difference in transmission obtained by the two methods.

Conclusions

The Luther and Forbes and Winther filters can both be quite efficient, but are very sensitive to the hydrogen ion concentration. Since it is impossible to be certain that any dye used in the preparation of a filter is precisely the same as that used by the original observer, all filters must be tested before use, and modified if necessary. It seems curious that the extreme sensitivity to the hydrogen ion concentration has not been previously noted in this connection. There are also certain other general objections to filters of this "chemical" type. The amount of light transmitted by them is never very high, and in fact frequently falls below the limit of utility. Again the fact that such substances as have sharp transmission bands must therefore have

sharp absorption bands of the "Photochemical" type, indicates the possibility of photochemical reaction which in course of time would change the transmission of the filter. Such filters as the Goerz glass and, for another region of the spectrum, the thin silver film, suffer from the disadvantage that they are not always homogeneous. The only safe method of procedure for all those filters is to measure the transmission before, and with filters of the chemical type also after, each experiment. The production of clear quartz has been so greatly improved in the last few years that there seems no reason why the division of the regions of the spectrum in the ultra-violet should not be made mechanically, by stopping off all except the required band from the light passing through a large quartz prism. This method has been used to isolate bands in the extreme ultra-violet, where the dispersion is high.[1]

The author desires to express his gratitude to Professor A. J. Allmand for his interest and suggestions during the course of this work.

University of London,
Kings College.
July 6, 1927.

[1] Cf. Kuhn: Compt. rend., 177, 956 (1923).

THE VAPOR PRESSURES OF METHYLENE CHLORIDE

BY J. H. PERRY

In working with mixtures of the chlorinated products of methane, the value of a knowledge of the vapor pressures of each member of the series is readily apparent. A comparatively large amount of vapor pressure data have been recorded in the literature for carbon tetra-chloride, chloroform, methyl chloride, and methane. There are however, very few data to be found on the vapor pressure of methylene chloride. Rex[1] has recorded four values of the vapor pressure at: 0°, 10°, 20°, and 30°C., but the methods of purifying the material used and the detailed conditions under which these data were obtained are not all that might be desired. The normal boiling point of methylene chloride is given in various handbooks and tables of constants as 41.6°, 40.0°, and 41.1°C. International Critical Tables p. 176 give 40.1°C. as the boiling point of methylene chloride, but the original sources of these data are obscure as to the details of the measurements. It has therefore seemed worthwhile to record here the vapor pressure data which were secured by the writer in the temperature range: 186.1° Absolute to 311.5° Absolute, covering a pressure range from less than one millimeter to about 715 millimeters.

Where, as in this case, the substance to be purified is one of a series of homologs and is to be separated from them, low pressure distillation is perhaps the best method to use, since at low pressures, the ratio of the vapor pressure of the more volatile substance to that of the less volatile is usually much greater than at high pressures and hence a separation may be more readily effected than where the ratio is smaller.

Methylene chloride obtained from the Research Laboratory of the Eastman Kodak Company was used in this work. It was further purified in the following manner: it was shaken with concentrated sulfuric acid several times, separated and then fractionated four times. For the reasons given above, all fractionations were carried out at low temperatures.

As a test of the purity of this material, use was made of the fact that the vapor pressure of a pure substance does not change as the ratio of the gas and liquid volumes is changed. This method of determining the purity of a substance is generally accepted as a criterion of purity. This test, as used in these experiments, in no case showed a variation of more than one millimeter and in the majority of cases the variation was less than one-half of one millimeter. Since the ice point is the most reproducible, the vapor pressure at this temperature was investigated very carefully, varying the ratio of gas and liquid volumes, and using several different, freshly prepared ice baths made of clear shaven ice and distilled water. A vapor bath of boiling ethyl bromide[2] was used to determine the vapor pressure of methylene chloride in the neighborhood of its normal boiling point, i.e., at 38.40°C.

[1] Rex: Z. physik. Chem., **55**, 358 (1906).
[2] Boiling point of ethyl bromide = 38.4°C Int. Crit. Tables.

The temperatures above −10.0°C. were measured with a mercury thermometer graduated in tenths of one degree and which had been carefully calibrated at several points in the range in which it was used in this investigation. The temperatures below −10.0°C. were measured with a calibrated pentane thermometer. The constant temperature baths used, were: thermostated water bath, and a bath of pentane cooled with liquid air to the desired temperatures. This latter bath was contained in a well-evacuated double Dewar flask the thermal leak of which was extremely small. The heights of the manometer columns were measured with a Gaertner cathetometer. The readings were corrected for latitude and reduced to 0°C.

The vapor pressures as obtained from two samples of methylene chloride by the purification described above are summarized in Table I and are shown graphically in Figure 1. It will be seen from this curve that the vapor pressure measurements in the two sets of experiments are in good agreement. The normal boiling point as determined by extrapolating a large-scale curve, is 313.7° absolute or 40.67°C.

TABLE I

Vapor Pressures of Methylene Chloride

Temperature (°Abs.)	Vapor Pressure (mm. Hg at 0°C	Temperature (°Abs.)	Vapor Pressure (mm. Hg at 0°C)
186.1	0.0	260.0	71.2
196.0	0.4	263.4	85.5
210.1	1.95	268.1	113.3
223.1	5.7	273.1	142.4
232.1	11.5	281.1	209.6
233.1	12.7	290.2	315.1
235.35	14.25	290.3	315.6
237.5	16.4	292.8	349.2
239.0	18.3	293.3	355.1
241.1	21.6	296.7	410.0
243.7	25.7	297.6	424.2
248.7	36.6	298.8	441.0
253.1	47.7	299.6	460.2
256.8	59.5	300.3	468.2
		311.50	715.8

In Table Ia there are given, for purposes of comparison, the data of Rex together with the results of the writer at the temperatures investigated by Rex.

TABLE Ia

Temperature °Abs.	Vapor Pressure mm. Hg at 0°C	
	Perry	Rex
273.1	142.4	147.4
283.1	231.5	229.7
293.1	353.5	348.9
303.1		511.4

In column I of Table II there are given values of the vapor pressures of methylene chloride taken from a large-scale vapor pressure curve at five degree intervals. In the second column, logarithms of these vapors pressures; in the third column, the absolute temperatures; and in the fourth column the reciprocals of these temperatures.

TABLE II

Data from the Vapor Pressure Curve

Vapor Pressure mm. Hg at 0°C.	Log Pressure 10	Temperature °Abs.	$1/T \times 10^3$
2.0	0.3010	210.0	4.7619
4.2	0.6233	220.0	4.5454
9.6	0.9823	230.0	4.3478
20.6	1.3139	240.0	4.1667
39.4	1.5955	250.0	4.0000
71.2	1.8525	260.0	3.8462
122.0	2.0864	270.0	3.7037
200.0	2.3010	280.0	3.5714
312.5	2.4949	290.0	3.4483
465.0	2.6675	300.0	3.3333

In Fig. 1 the logarithms of the vapor pressure are plotted against the reciprocals of the absolute temperatures. It is seen that the data may be represented very well by a straight line except for the highest values of $1/T$ at which measurements were taken. Here the curve begins to toe down very gradually. In the same figure, there are shown the curves of: Vapor Pressure (mm Hg) versu sthe temperature on the absolute scale. Using the approximate Clapeyron equation:

$ML = (2.303_R)\ (T_1T_2)/(T_2 - T_1) \log_{11} P_{2/P_1}$ where ML is the molecular heat of vaporization, the heat of vaporization at the normal boiling point has been calculated to be about 7020 calories. By dividing this datum by the boiling point on the absolute scale (313.77), the Trouton coefficient $ML/T_{b.pt.}$ is found to be equal to (22.4). The values of this coefficient calculated from the two formulae of Nernst are:

$8.5 \log_{10} T_{b.pt.} = 21.22$ and $9.5 \log_{10} T_{b.pt.} - 0.007\ T_{b.pt.} = 21.53$ and from Wartenberg's formula: $7.4 \log T_{b.pt.} + 1.935 = 20.51$.

The ratio of the absolute temperatures that correspond to vapor pressures of 760 mm. and 200 mm. is 1.114, which is the value shown by Ramsay and Young[1] to correspond with normal liquids. These considerations would seem to show that there is very little, if any association of methylene chloride in the liquid state. The formula of methylene chloride in both the gaseous and the liquid state may be considered to be CH_2Cl_2.

[1] Ramsay and Young: Z. physik. Chem., 1, 249 (1887).

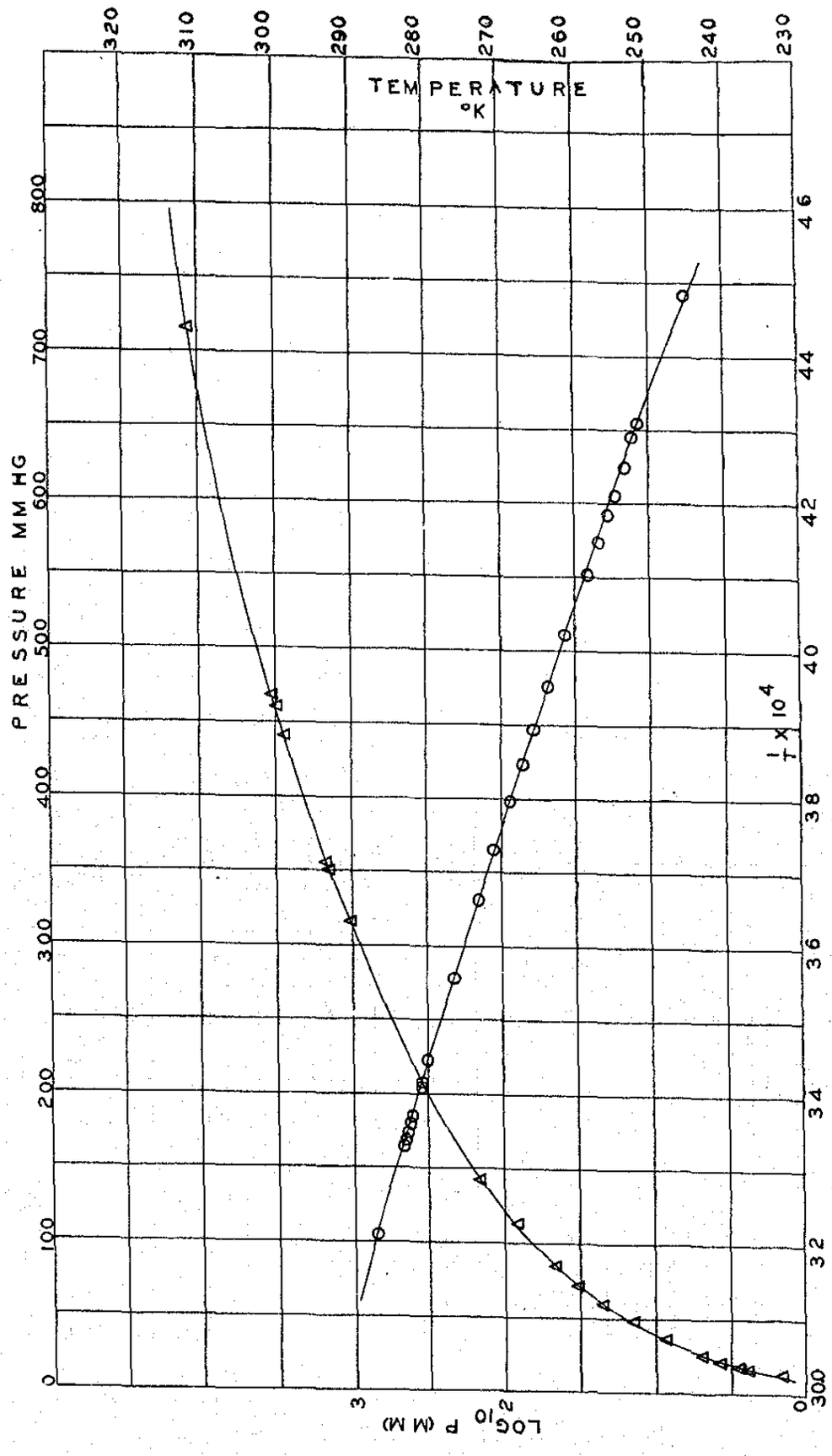

TEMPERATURE °K
320
310
300
290
280
270
260
250
240
230
PRESSURE MM HG
800
700
600
500
400
300
200
100
0
$\frac{1}{T} \times 10^4$
46
44
42
40
38
36
34
32
$\log_{10} P$ (M M)
3
2
0
300

FIG. 1

The following relation has been proposed by Prud'homme:[1]

$\frac{T_f\ (T_c - T_f)}{T_b\ (T_c - T_b)} = 1.00$, where T_f, T_c, and T_b are: the freezing point (-96.7),[2] the critical point, and the boiling point respectively on the absolute scale of temperature, there is obtained for the critical temperature of methylene chloride, the value 215.7°C.

This calculated value may be compared with the value obtained experimentally by Nadejdine[3] of 245.1°C.

Summary

The vapor pressures of pure methylene chloride has been obtained through a temperature range from 186.1° Abs. to 311.5° absolute and a pressure range from less than one millimeter to about 715 millimeters. The normal boiling point has been found by extrapolation to be 40.67°C. The latent heat of vaporization, calculated from the modified Clapeyron equation is 7020 calories per gram mole (at the normal boiling point). The critical temperature has been estimated to be 215.7°C. as compared with the single experimental value of 245.1°C. given in the literature.

Wilmington, Delaware.

[1] Prud'homme: *J. Chim. phys.*, **18**, 359-61 (1920).
[2] Bull. Soc. belg., **25**, 300 (1911).
[3] Nadejdine: J. Russ. Phys. Chem. Soc., **14**, 157 (1882); Beibl., **7**, 676 (1883).

ON THE CAUSES OF SOLUBILITY: SURFACE FORCES IN A SYSTEM CONSTITUTING A PAIR OF PARTLY MISCIBLE LIQUIDS

BY ROWLAND MARCUS WOODMAN

The work described in the present paper was done primarily with the view of subjecting to experimental verification a theory concerning the distribution of a consolute liquid between two immiscible solvents, this aspect of the case forming the basis of a subsequent communication; a system of this type, namely, water-acetic acid-toluene, has been carefully investigated at 25°C. by a combination of synthetic and analytical methods.[1]

The investigation contemplated was the measurement of the surface tensions between the separate layers and air, and the interfacial tension between the layers,[2] for various equilibrium mixtures of the system as a gradual approach to the critical point was made.

Experimental

Accurate measurements of the surface forces were not aimed at, and would hardly have been possible in such a system without the use of complicated apparatus.

An essential feature of work on these systems must be quickness, and, partly for this reason, and partly because an apparatus of convenient bore was needed to reduce manipulation for measurements of both kinds of tensions, a straight Traube stalagmometer[3] was used. This was found to give an absolute error of anything up to 0.25 dynes/cm. in making measurements over the range 20-80 dynes/cm. for liquid/air tensions on the same sample, but a less error for the liquid/liquid tensions measured; more consistent results were obtainable for pure liquids. To this error, that due to the method of calculation must have been sumperimposed.

The method of calculation was as follows: the number of drops (n) was calculated for the known volume (x) of the bulb at 25°C.; then $xd/n = w$ was the weight of one drop, where $x/n = v$ = the volume of one drop, and d = the density of the liquid under observation. The desired tension being σ, $w = Kr\sigma$ by Tate's law,[4] where K = a constant and r = the tip radius. If, now, w_1 and σ_1 are the corresponding values[5] for pure water at 25°, $\sigma = \sigma_1 vd/w_1 = \sigma_1 w/w_1$.

[1] Woodman: J. Phys. Chem., **30**, 1283 (1926).

[2] It was perceived at the outset that an investigation of this type would lead to results as regards the causes of solution; since doing most of this work, a similar suggestion has been noticed in Rideal's new book: "Surface Chemistry," 107 (1926).

[3] Traube: Ber., **20**, 2644 (1887); Freundlich: "Capillary Chemistry," 22 (1926).

[4] The assumption of proportionality, which is questioned by Harkins and Humphery: J. Am. Chem. Soc., **38**, 228 (1916); Harkins and Brown: 246 (1916); and Lohnstein: Z. physik. Chem., **64**, 686 (1908); **84**, 410 (1913), has been made by Tate: Phil. Mag. (4), **27**, 176 (1864); Worthington: Proc. Roy. Soc., **32**, 362 (1881); Rayleigh: Phil. Mag., **48**, 321 (1899), and, later, from accurate experiments—no doubt due to the accidental choice of tip radii which give proportionality—by Morgan and Cann: J. Am. Chem. Soc., **33**, 1060 (1911), etc.

[5] σ_1 was obtained by extrapolation of Harkins's result at 20°C.

For interfacial tensions, the equation used was $\sigma_{12} = \sigma_1 v(d - d_1)/w_1$, where σ_{12} is the desired tension, v the calculated volume of one drop, and d and d_1 the densities of the dropping and the second liquid respectively, w_1 being, as before, the weight of a drop of water from the same tube in air.

The results are given in Table I.

TABLE I

(all results at 25°C.).

Surface tension of water[1] = 72.04 dynes/cm.
Surface tension of toluene = 25.3 dynes/cm.
Surface tension of acetic acid = 23.3 dynes/cm.

No. of Expt.	Wt. % of acetic acid in aqueous layer[2]	Surface tension: (dynes/cm.) Aqueous layer (σ_1)	Surface tension: (dynes/cm.) Toluene layer (σ_2)	Interfacial tension: (dynes/cm.) Observed (σ_{12})	Interfacial tension: (dynes/cm.) Calculated ($\sigma_1 \sim \sigma_2$)
1	0.00	63.6	25.5	37.6	38.1
2	21.38	42.6	25.2	17.1	17.4
3	30.87	38.5	24.9	12.8	13.6
4	37.69	35.3	24.7	10.9	10.6
5	47.50	32.5	24.7	7.5	7.8
6	58.05	28.9	24.5	4.8	4.4
7	64.86	26.7	24.4	2.6	2.3
8[3]	67.70	25.6	24.2	1.5	1.4
9[3]	69.71	25.3	24.2	1.2	1.1
10[3]	70.55	24.7	24.1	0.7[4]	0.6
11[3]	66.68	23.5	24.0	Streams	[0.5]
12[6]	60.54[5]	23.4	23.8	do	[0.4]

[1] Calculated from Harkins's value (loc. cit.).
[2] This column is given as a reference to Table II of the previous paper, where analyses and densities of the layers will be found (Woodman: loc. cit.).
[3] Capillary junction above cylinder junction (see later).
[4] Nearly streams.
[5] New equilibrium: Wt. % of acid in aq. layer ($D^{25}_4 = 0.98185$) = 60.54. Wt. % of acid in tol. layer ($D^{25}_4 = 0.95299$) = 50.98.
[6] Capillary junction below cylinder junction (see later).

Antonow[1] and Reynolds[1] have formulated a rule which states that the interfacial tension existing between the mutually saturated phases obtained by shaking together two partially miscible liquids, is equal to the difference in the surface tensions of the two phases. This rule is shown by Rideal to have some theoretical basis, but to be exact only when the phases possess the same density.[2]

[1] Antonow: J. Chim. phys., 5, 372 (1907); Reynolds: J. Chem. Soc., 119, 466 (1921).

[2] Rideal: loc. cit., 97; it is doubtful, however, how the interfacial tension between two liquids of the same density could be measured. The author of this paper thinks that any mutually saturated phases of the same density got by shaking together any number of liquids are impossible, equalisation of densities in such a case occurring only at a critical solution point. Two liquids of the same density, on the other hand, shaken together, would give two mutually saturated phases, differing more or less in density, and thus obeying the Antonow-Reynolds's rule less or more exactly, depending on the combined effects of the extent of miscibility and the deviation from the simple mixture law.

The results quoted, whilst, in common with most similar measurements, not showing a high order of accuracy, yet point to the fact that the Antonow-Reynolds's rule holds in the case of three liquids which constitute a partly miscible pair;[1] in many of the comparisons, the observed divergences could be accounted for by the combined effects of errors of experiment, method of calculation and difference of phase density. It may thus be stated that each equilibrium represents the mutually saturated phases resulting from shaking together two partially miscible liquids.

The most probable assumption is that these two liquids are a mixture of water and acetic acid, and toluene and acetic acid; and, as the rule is followed in all equilibria, it must be assumed in every case, that, on shaking together the three liquids, two new and definite liquids—depending for composition on the partition coefficient of the consolute between the two immiscible liquids—are momentarily formed (corresponding to, say, water and toluene), and that these two definite liquids, being, to some extent, miscible, mix to form the equilibrium phases without loss of identity (corresponding to the saturated phases of water and toluene). When these definite liquids have such a composition that they mix to give mutually saturated phases of identical properties and composition, the interfacial tension, incidentally, being zero, the critical point has been reached.

The results given also show that the surface tensions of the phases tend to coincide as the critical point is approached. The tension of the toluene phase decreases little, but that of the aqueous phase greatly, though the rate of decrease becomes less as the critical point is reached. This behaviour of the tension liquid/air is, because the Antonow-Reynolds's rule is followed, repeated in the case of the interfacial tensions, which tend to decrease rapidly at first, but more slowly near the critical solution point.

The tensions of the aqueous phases are, up to a certain point, greater than those of the toluene layers; beyond this the reverse holds. An important inference may be drawn from this behaviour: the tensions of such a system may coincide and then reverse positions as regards magnitude, (and, as a necessary reflection of this behaviour, the tension between the phases may be zero), *before* total solution occurs.

There is, in a system such as the present, nothing really remarkable in this behaviour: the surface tension of the consolute (acetic acid), is less than that of water or toluene, and the phases contain little water and much acid and toluene where this phenomenon occurs. In order to see if this behaviour were due to errors of measurement, however, a qualitative test was used[2]: capillary tubes, of such length as to reach into, and end in, the toluene phase, were introduced into cylinders containing the mixtures at 25°. The line of demarkation of the phases in the tubes was concave upwards and definitely

[1] From these and similar results, it might be argued that two mutually saturated phases formed by any number of liquids or solutions shaken together will obey this rule; it is also conceivable that in liquid systems containing more than two layers, the rule will hold between any two adjacent layers.

[2] Goard and Rideal: J. Chem. Soc., **127**, 780 (1925).

above that in the cylinder up to experiment 10; the capillary junction of the two phases was practically on a level—probably slightly above—with that in the cylinder in case 11, showing that an error of about 0.5 dynes/cm. had been made in estimating the interfacial tension by difference; but, in the last case, the capillary junction was far below the outer and concave-downwards junction. The tensions of the phases first coincide, therefore, between the last two results.

A direct consequence of the results is that coincidence of the liquid/air tensions—with the resultant reduction to zero of the liquid/liquid tension—is shown to be not necessarily the main criterion of solution. Other properties play a decided part, and must also coincide at the same time. In addition, as other work has also tended to show,[1] and as the present results[2] show as clearly as can be expected from the degree of accuracy attained, the zero value of the interfacial tension must coincide, apparently, with a zero rate of alteration of tension with respect to concentrations. If any system obeys the Antonow-Reynolds's rule, then, as the alteration in the interfacial tension is, to a great extent, a mere reflection of the alterations in the surface tensions of the phases, the rate of change of these tensions with respect to concentration must also be zero at the critical point.

Summary

The surface forces existing in a system constituting a pair of partly miscible liquids have been measured, and the phases have been to obey the Antonow-Reynolds's rule.

It is shown that coincidence in the values of the surface tensions of the phases, with a zero interfacial tension, are, of themselves, not sufficient to cause total miscibility; other properties must coincide at the same time, and, in addition, the rates of change of the three tensions with respect to concentration must be zero.

Horticultural Research Station,
University of Cambridge,
England.
April 8, 1927.

[1] Freundlich: loc. cit., 96 et seq.

[2] The calculated results in brackets are not negative, but are given on the assumption that the Antonow-Reynolds's rule holds irrespective of which phase has the maximum tension; thus it is not intended to imply that the interfacial tension becomes negative in the neighbourhood of a critical solution point, as some seem to infer, (*vide* Freundlich: loc. cit., 100).

248-164

COMPOSITE YELLOW*

BY JACOB PAPISH AND F. E. AGEL

In 1871 while participating in a discussion on the existence of composite yellow, Lord Rayleigh[1] described a method for the production of such a color. The method consisted in bringing together in a glass cell an alkaline solution of litmus and a solution of potassium chromate. "A mixture of these two liquids *in proper proportions, easily found by trial,*[2] isolates the green and extreme red rays with considerable perfection, and exhibits in a high degree the phenomenon of dichromatism." Lord Rayleigh further stated that another liquid which answers the same purpose can be prepared by mixing solutions of chromium chloride and potassium dichromate.

Experiments were carried out with the solutions suggested and the following difficulties were encountered: Mixtures, the concentration of which had been adjusted to absorb spectral yellow light, were distinctly red in color. If on the other hand the mixtures were diluted so that they looked yellow by transmitted light, they were found to be transparent to spectral yellow. Unsatisfactory results were similarly obtained when instead of mixing the two solutions they were placed each in a glass cell and the combination held in the front of a suitable light.

It is known that compounds of neodymium exercise strong absorption in the yellow spectral region. A solution of neodymium chloride containing approximately an equivalent of 4 gm. of Nd_2O_3 per 100 cc. was prepared and placed in a cell 2 cm. thick. This was joined with the aid of rubber bands to a 3 cm. cell filled with a saturated solution of potassium chromate. The combination when viewed by transmitted daylight appeared distinctly yellow. The same color was observed when diffused light from an incandescent bulb was employed instead of daylight. It was not difficult at all to notice with the aid of a pocket spectroscope the absence of spectral yellow. This fact can be corroborated strikingly in the following manner:

If on the grid of a Meker burner a piece of copper wire and a small lump each of a salt of sodium and lithium be placed in a row and the burner lighted, the flame when viewed with the naked eye will be seen to consist of three streaks colored green, orange-yellow and red, respectively. Now if the cells with the solutions of neodymium chloride and potassium chromate be placed between the flame and the eye of the observer the yellow light will be absorbed and only the red and the green streaks will be visible. In repeating this experiment it should be borne in mind that if too much of the sodium salt is

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[1] Nature, **111**, 234 (1871).

[2] The italics are ours.

volatilized the orange-yellow light will be correspondingly intense and it will not be totally absorbed by the combination of liquids but merely reduced in intensity.

While the work described in this article was in progress, there was in our laboratory a student who suffered from a peculiar kind of color blindness: She was insensitive to green, but saw all the rest of the spectrum. She was able to distinguish between the composite yellow and the yellow of a potassium chromate solution, though no one else in the laboratory could. This seems to indicate that certain individuals do have a primary sensation of yellow. When the cell combination with the two liquids was held against white light and the student was asked about the color, she declared it was "brownish red."

Cornell University.



NEW BOOKS

Acetate Silk and Its Dyes. *By Charles E. Mullin. 22 × 14 cm; pp. 473. New York: D. Van Nostrand Company, 1927. Price: $6.00.* In the preface we read that "the author has no hope that all who peruse this volume will at once be able to obtain all of the desired results on the various forms of acetate silk, and has merely endeavored to bring the available and rather widely scattered information on this subject into a concise and convenient form for the busy chemist, dyer, and textile technologist. Dyeing is not learned from books alone, but it is hoped that the present volume may aid the busy mill man to make such experiments as will enable him to solve his own problems on dyeing acetate silk. After all, the really successful dyer is the man who can take an idea, work it out, and apply it to his own problems," p. 3.

In the introduction Professor Olney says: "Luster as a desirable quality of textile materials has been prominently before the purchasing public for several thousand years. During most of this period dependence has been placed upon natural silk for the purpose of producing it, but the past half century has witnessed an interesting, and we might say, revolutionary encroachment upon the domain of the silk worm.

"The luster produced upon cotton yarn and cloth by subjecting it, under tension, to the action of concentrated caustic soda solution (mercerization) has been and is still a very important factor in the production of beautiful textile materials, but the luster produced in this manner has not been nearly so great or its development and use so spectacular as that of the so-called artificial silks, which in many instances far exceed in luster the natural silks.

"These extremely lustrous fibers have all been produced in a manner which imitates the silk worm, as far as mechanism of process is concerned, but chemically they are entirely different; and the final fiber substance is not at all comparable with true silk in composition. For this latter reason, they are not, strictly speaking, artificial silks. As a consequence of this misnomer, various attempts have been made to devise a generic name which would not convey an erroneous idea, but which could properly be used to designate any type of fiber produced by forcing a semi-liquid substance through a very fine orifice, with subsequent hardening. Among the names suggested, that of "Rayon" appears to have met with the greatest favor, and at the present time it is being quite generally used by both textile manufacturer and consumer," p. 9.

The chapters are entitled: general considerations; the development of the rayons; preparation of cellulose acetate and acetate silk; general properties of acetate silk; other rayons, and natural fibers; identification of the various rayons; detection of mercerized cotton; dyeing the older rayons; dyeing properties of acetate silk; desizing, scouring, bleaching, and tinting; basic dyes on acetate silk; dyeing by precipitation; mordanting acetate silk; acid and mordant dyes on acetate silk; acid and mordant dye patents; direct cotton, sulfur and vat dyes on acetate silk; special components for the developed colors on acetate silk; swelling agents or solvents in dyeing acetate silk; dyeing acetate silk by saponification; the ionamines; the dispersol type of dyes; the celatene, duranol, dispersol (brand), azonine direct, cibacete, celanthrene, cellacete, and other dispersol type dyes for acetate silk; dispersol type dyestuff patents; prints and discharges on acetate silk; dyeing union materials; basic dyes on acetate silk unions; acid and mordant type dyes on acetate silk-cotton unions; sulfur dyes on acetate silk-cotton unions; vat dyes on acetate silk-cotton unions; developed colors on acetate silk unions; the ionamines on acetate silk-cotton unions; dispersol type dyes on acetate silk- cotton unions; direct cotton dyes which leave acetate silk white; dyeing acetate silk and wool or true silk combinations; clearing acetate silk unions and stripping acetate silk; mode of application; dyeing troubles and faults; sizing and finishing acetate silk.

"Acetate silk, the infant prodigy of the textile industry, by reason of its new, valuable, and extremely interesting chemical, physical, textile, and dyeing properties, has practically forced itself upon the attention of every branch of textile manufacturing. Without doubt

the unique dyeing properties of this fiber are foremost in its favor at the present time, for while it offers many other and very interesting points for its support, no other fiber can even approach it for most white or two-color effects when in combination with the older and better known fibers.

"At the present time all the rayons are in unprecedented demand, but acetate silk by reason of its dyeing properties alone, holds a certain definite field of usefulness upon which none of the older rayons (nitro, viscose, and cuprammonium) can even encroach. Yet only a few years ago it was these very dyeing properties, or rather with the information then available, its lack of dyeing properties, that restricted the use of this wonderful new fiber. The fact that both the fiber and its dyeing methods, as well as most of the dyestuffs themselves, are very new, the two latter having been developed especially for this particular fiber, renders technical information on these subjects of special interest, especially to all textile chemists and dyers, at this time.

"We are all more or less familiar with the older varieties of regenerated cellulose rayon which have come into such wide use in recent years, their individual and collective properties, methods of dyeing, etc. Acetate silk is an entirely different product in that it is a cellulose ester (acetate) and not a regenerated, modified, or hydrated form of cellulose, as are the older and better known rayons. There is no more relation between the older rayons and acetate silk in many of their properties than there is between glycerol and olive oil, or alcohol and ethyl acetate. In this instance we may compare the older rayons to the glycerol and the olive oil to acetate silk. Cellulose is the basic constituent of all of our present rayons, acetate silk included; but in the acetate silk the cellulose is combined with acetic acid to form an ester, just as in olive oil the glycerol is combined with the fatty acids to give the ester which we know as olive oil. With this in mind, we would expect quite different properties in the new product, acetate silk, and we are certainly not disappointed. No dyer or chemist would attempt to successfully substitute glycerol for olive oil, or alcohol for ethyl acetate, in very many processes, or *vice versa*. No more can he with uniform success dye acetate silk by the methods successfully applied to the older rayons or cotton," p. 13.

"The name rayon has been applied as a class designation to the whole group of fibers formerly known as artificial silks. However, as pointed out by Davies, American Dyestuff Reporter, **15**, 197 (1926), this does not satisfy the technical mind, since the fibers produced by the different chemical methods possess different chemical, physical, and dyeing properties. It is therefore customary for the technical man to refer to the different rayons under the various names which describe the chemical processes involved in their manufature, and he therefore speaks of viscose silk, cuprammonium silk, nitro silk, and cellulose acetate silk, acetyl, or acetate silk, as we will call it," p. 13.

"That wide differences in the properties of the finished product, both as cellulose acetate and acetate silk, do exist is fully recognized by all those familiar with the industry. An instance of this is the differences in our two best known acetate silks, Lustron and Celanese. Both of these types have acetylation values higher than cellulose diacetate and lower than the triacetate, but Lustron is more highly acetylated than Celanese.

"In the manufacture of Lustron, the cellulose acetate is dissolved in a combination of tetrachlorethane and some cheaper solvent, or in chloroform. This solution is forced through the spinneret into a hydrocarbon, such as kerosene, in which the solvent is dissolved and the cellulose triacetate (Lustron) fiber precipitated. In the manufacture of Celanese, on the other hand, the cellulose acetate is dissolved in acetone or a similar cheap, volatile solvent, and the fiber subsequently formed by the evaporation of the solvent. Most dyers soon become familiar with the differences in the two products, which will be considered more in detail as we proceed," p. 23.

"Celanese contains only about two acetate groups per cellulose molecule and therefore corresponds closely to cellulose diacetate; but it is undoubtedly produced by hydrolysis," p. 25, of a higher acetylated product. "The chloroform-soluble, acetone-insoluble products of the direct acetylation of cellulose are designated *primary acetates*, while the acetone-soluble product resulting from the hydrolyzing or 'ripening' process are called secondary

acetates," p. 26. Apparently Craik's work on the cellulose nitrates will apply to the cellulose acetates (Fifth Colloid Symposium Monograph)"

"Hess attributes the variable solubilities of cellulose triacetate in its different forms as due to the influence of small quantities of impurities. The triacetates which are soluble in chloroform or tetrachlorethane show a specific rotation with sodium light of approximately $-20°$ in these solvents and $-50°$ in pyridine. They can be produced in the form of large crystals from solutions in tetrachlorethane or in ethylene-tetrachloride. Presumably these acetates form molecular combinations with the solvents. The lower acetates, soluble in acetone, show a specific rotation, with the same light, of only about $-21°$ in pyridine. He also states that the ideas of polymerisation and depolymerisation of the cellulose molecule are untenable, and that it reacts as a chemical unit $C_6H_{10}O_5$, rather than as $C_{10}H_{20}O_{10}$. Herzog and Kruger report that their experiments indicate that cellulose acetate disperses in acetone when the diameter of the particles is less than $20\mu\mu$, in ethyl acetate when less than $5\mu\mu$, and in epichlorohydrin when less than $35\mu\mu$.

"The following is a list of some of the most common chemicals which have considerable solvent power for some or all of the cellulose acetates. No attempt will be made to enumerate the non-solvents, for in many cases, in the presence of other compounds, usually cellulose acetate solvents, some of the so-called non-solvents aid materially in the solution of the acetate. The compounds enumerated below should never be present in scouring baths or dry-cleaning solvents for use upon materials containing acetate silk.

"Chloroform, acetone, tetrachlorethane, alcohol of various strengths, phenol, cresols, light acetone oil, acetic acid, nitro-benzene, pyridine, aniline, triacetin, toluidine, xylidine, mono-, di- and epi-chlorhydrin, acetylene, tetrachloride and ethyl acetate, benzyl alcohol, diacetone alcohol, cyclohexanone and other cyclic ketones of the same series," p. 38.

"Parker and Jackson investigated the strength of different materials by means of the Mullen bursting test. Wool, true silk, viscose, and Celanese fabrics, both woven and knitted, showed a large and fairly regular fall in strength as the humidity increased, although when wetted, the loss with true silk was only half the loss with viscose, which was affected most. Celanese and wool showed losses intermediate between those of true silk and viscose. Cotton and mercerized cotton showed a slight increase in bursting strength with rising humidity, while linen was 25 per cent stronger wet than when dry. In all cases the change in strength on wetting appears to take place rapidly. Pieces tested immediately after wetting and those tested after soaking for two days gave the same strength. The strength changes are only temporary, all fabrics reverting approximately to their original strength when reconditioned at, say, 70 per cent relative humidity," p. 50.

"Lustron and Celanese may be distinguished by boiling a few threads of the sample in 10 or 15 cubic centimeters of the 2*a* Methylene Blue solution as above, acidified with 1 or 2 cubic centimeters of acetic acid. Wash the dyed samples well in water. The Lustron retains a deep blue color, but the color of the Celanese washes out to a comparatively pale blue. This difference is entirely due to, and is typical of, the affinity of the two fibers for the basic dyes. While the basic dyes have a greater affinity for Lustron than any other known textile fiber, this is decidedly not the case with Celanese. Dort states that this test is not always reliable," p. 76.

"Nitro silk is also known as Chardonnet, nitrocellulose, collodion, pyroxylin, du Vivier, Frankfurter, soie de France, Meteor, Strehlenert, Besançon, Hungarian, Tubize, and Lehner artificial silk. Nitro silk, as the variety of names indicate, is manufactured in many different plants and while all are similar in appearance, in most instances the product of each plant differs in some slight degree from that of the other plants. Nitro silk is usually more lustrous than natural silk, harsher and without the characteristic feel of true silk. It has been stated that the original undenitrated Chardonnet silk more closely approaches the present acetate silks in many of their desirable properties, than any other type of rayon.

"Nitro silk has a great affinity for the basic dyes, whereas viscose and cuprammonium are best dyed by substantive dyes. Nitro silk is dyed even to deep shades by the basic dyes without mordanting, probably due to its combined oxycellulose and hydro-cellulose content, but viscose and cuprammonium silks should first be mordanted with tannin and tartar

emetic before applying the basic dyes. The fastness of the basic dyes on nitro silk to washing is increased by top-mordanting them with tannin and antimony in the usual manner. On account of the high affinity of nitro silk for the strongly basic dyes, acetic acid is frequently used as a retard and to aid leveling in applying them to this fiber. The weakly basic dyes show much less affinity for nitro and therefore must be applied in short baths of high concentrations, or on a mordant, to give deep shades.

"In general, nitro silk has less affinity for the direct cotton dyes, as a class, than either viscose or cuprammonium. In fact, it has been stated that the affinity of the direct cotton dyes for all of the rayons, acetate included, is just the reverse of the affinity of the basic dyes as given above. However, the direct dyes are frequently used on nitro silk, especially for light and medium shades. The vat and sulfur dyes may also be used on nitro silk but in applying the sulfur dyes, care must be taken to avoid loss of luster and strength," p. 99.

"Viscose silk is also known as vistra, staple fiber, xanthate, Luna, Stettiner, Du Pont and Celta silk, and is prepared from solutions of mercerized cellulose in caustic soda and carbon disulfide. It is a regenerated cellulose with a fine glossy appearance. Its affinity for dyestuffs is similar to that of mercerized cotton and it appears to have an intermediary affinity, for both the basic and direct cotton dyes, between nitro and cuprammonium silks. In other words, it has more affinity than nitro silk for the weakly basic dyes, but less affinity than the cuprammonium. Basic dyes may be used for pale and medium shades without a mordant, but for heavy shades it should be mordanted and dyed in the presence of acetic acid," p. 100.

The author is hopelessly weak on all points connected with the theory of dyeing and apparently has not heard of adsorption, though he does use the term peptization. "While the solution theory of dyeing acetate silk appears to favor the mechanical theory of all dyeing, it does not necessarily prove it. In truth, the very fact that acetate silk is not dyed by the direct cotton and other dyes of the acid type has been used to assist the proof of the chemical theory of dyeing cellulose. Undoubtedly more than one factor enters into the dyeing of acetate silk, just as it does into dyeing all other textile fibers. The high affinity of the color base and of compounds containing the strongly basic amino group, as well as many other basic compounds, for acetate silk, which is certainly of an acidic character, most certainly indicates that chemical factors play some, and possibly, the most important part.

"The fact that dyes which are soluble in ethyl acetate as a rule dye acetate silk does not prove that dyeing acetate silk is a solution phenomenon. There is nothing to prevent the formation of compounds between the base of the dye and the acidic radicle of the solvent (ethyl acetate) in at least some of the cases. Without doubt where the solubility of the dyestuff in the fiber is greater than its (dyestuff) solubility in water, this solubility factor plays the important part in dyeing, but unless some form of chemical change or combination takes place, we would hardly expect these dyes applied by solubility alone to be fast to washing. In the case of the dispersol dyes, the method of solubilizing or dispersing the comparatively insoluble dyestuff is an important factor in its application and fastness, but this hardly explains the fastness of the strongly basic dyes on Lustron, the most acidic textile fiber of commerce.

"If dyeing acetate silk is entirely a solution phenomenon, why is it that very few compounds except those of a basic character or containing strongly basic groups, are soluble in acetate silk? A great many investigators appear to fear a chemical theory of dyeing any fiber, wool and silk included. They may look further and do worse than a chemical theory in many instances," p. 107.

"Haller and Ruperti report some interesting work upon the orientation of coloring matters within acetate silk and other fibers. When acetate silk is dyed at low temperatures with Para-Red it has a yellowish shade, the dye being uniformly distributed within each fiber. After immersion in hot or boiling water, the shade becomes redder and the dye agglomerates into larger particles. Similar results are obtained, although with greater difficulty (steaming under pressure is necessary), when Para-Red is obtained from naphthol AS instead of β-naphthol, or when aminoazobenzene is used instead of p-nitroaniline.

"Similar changes are observed in nitro silk dyed with the same dyes and also with Indigo, Thioindigo Red, and Indanthrene Blue. Nitro silk dyed cold with Naphthylamine Claret (α-naphthylamine coupled on the fiber with β-naphthol) contains the dye evenly distributed. When heated in water under one atmospheric pressure the dye agglomerated slightly without change of shade, but when heated for a prolonged period in boiling water or subjected to a short steaming under six atmospheres pressure, agglomeration becomes complete, the dye migrates towards the surface of each fiber and is deposited there as well-defined crystals which may be removed by washing and pressing, the fibers being thereby decolorized. Thioindigo Red dyed on nitro silk behaves similarly. Chrome Yellow, from lead acetate and a dichromate, dyed on nitro silk, is at first evenly distributed, but after steaming under four atmospheres pressure, agglomerates, and becomes orange, even in the absence of alkali, although no migration of the pigment occurs.

"Similar changes are observed by steaming dyed cotton, except that the agglomerated dyes migrate to the boundaries of the lumen in each fiber as well as to the cuticle, the migration, change of shade, and condensation or crystallization of the particles of dye being favored by prolongation of the steaming or rise of temperature. Vat dyes, Indigo and Thioindigo Red easily, and Indanthrene Red 5GK, Indanthreme Brilliant Violet RK, and Indanthrene Blue RS with greater and increasing difficulty, crystallize and migrate within cotton fibers to the lumen and cuticle when steamed, accompanied by a change in shade. Uncertain results are obtained by steaming cotton dyed with direct dyes.

"Alizarin Red dyed on cotton mordanted with aluminum acetate is evenly distributed within each fiber, but when steamed for an hour under a half atmosphere pressure the pigment agglomerates and migrates to the lumen and cuticle. That deposited near the cuticle is removed by washing with water, the fiber being left colorless. Under similar conditions the presence of Turkey-red oil considerably retards the agglomeration and migration, and the dye which migrates to the cuticle cannot be removed by washing. The decrease in fastness to rubbing produced by steaming cotton dyed with indigo is due to migration of the dye to the cuticle of each fiber.

"Haller reports work of a similar nature upon the color changes of the blue and violet benzidine dyes on cotton, wool, and acetate silk, especially on touching the dyed cotton with a hot iron. His experiments are stated to confirm the view that these dyes form colloidal solutions of different degrees of dispersion, the larger particles coloring the cotton fiber blue, the smaller corinth-red. Solutions of a low degree of dispersion are particularly sensitive to temperature changes or to variations in the medium employed. Thus, in hot dye baths, wool and cotton are dyed red by aqueous solutions; but on cooling, the color on the bottom becomes blue-violet. Alcoholic solutions hardly affect wool but dye cotton a permanent corinth-red.

"The effect of touching the dyed cotton with heated metal is to increase the degree of dispersion of the dye in the fabric, with a change of color from blue to red. The addition of hydrazine hydrate to aqueous Diamine Blue 3R solution causes a similar change, and the solution will then dye cotton corinth-red. The absorption of the dyes by fibrous alumina and barium sulfate indicates a fixed relationship between the degree of dispersion of the dyestuff and that of the absorbent. The surface of the absorbent plays a decisive part also when fibers are used, for swelling causes inner micellar surfaces to come into play, the difference in the sizes of these accounting for the different behavior of different absorbents.

"Wool and acetate silk, after swelling, have larger inner surfaces than cotton. Thus an alcoholic solution of Diamine Blue 3R causes swelling of acetate silk and dyes it corinth-red. After saponification with sodium hydroxide, washing the fiber, and acidifying, the color changes to blue, showing that during saponification the inner structural conditions are changed. The reddening of blue-dyed cotton is also produced by desiccation over sulfuric acid, but to a less extent than by heating. The observed color changes on heating, and drying may thus be connected with dehydration and simultaneous increase in the degree of dispersion of the dyestuff within the fiber." p. 116.

"Acetate silk has no affinity for the usual soluble salts of the metals used in mordanting the other textile fibers, such as chromium, aluminum or iron; nor will it take up their

hydroxides to any extent, either as precipitates or as colloidal solutions. However, as discussed under the mordants, it has recently been found that it does have an affinity for certain special salts of the mordanting metals, such as the thiocyanates, but these particular salts had not previously been used in mordanting, and the process is probably not yet highly successful on a commercial scale. It has no affinity for the tannins or other usual cotton mordanting agents." p. 120.

"While acetate silk has no affinity for the usual mordants, such as the cotton salts of iron, chromium, and aluminum, many mordant dyes may be applied to it without a mordant by virtue of their phenolic and ketonic properties," p. 167.

"Before leaving the theoretical discussion of acetate silk dyeing, it may be well to mention a difficulty encountered in the search for dyestuffs particularly suitable for use on acetate silk. When applied to acetate silk, many colors appear to be subject to "phototropism," a rather newly discovered property of some dyestuffs which is found almost only on acetate silk and which is not usually found in the same color on other fibers. Phototropism is the property of a color on the fiber to change in color or shade under certain lighting conditions. For instance, if the dyed silk is shielded from the light for a few minutes, on removing the shield, the color is lighter beneath where the shield covered, but darkens in a short time until it matches the surrounding color. This difficulty was encountered in the development of both the Ionamines and the dispersol type of dyes. While it is rare on other fibers, it is not entirely unknown, as for instance in the case of Fast Light Yellow on wool.

"Green and Saunders report that nearly all of the yellow amino-azo bases show this property on acetate silk, and though varied by substitution in the benzene nucleus, no definite relationship between the position of the substituents and the occurrence of phototropism can be traced. Apparently the greener the shade of the yellow, the more pronounced is its phototropism. The difficulty usually disappears when orange shades are reached.

"The cause of phototropism in certain azoic dyes on acetate silk has never really been satisfactorily explained, but Greenhalgh compares it with the desmotropism of *p*-nitrosophenol. In the case of *p*-nitrosophenol under certain conditions the compound is white and under others it is yellow. Analysis of the yellow product shows that it is not *p*-nitrosophenol but is quinone oxamine. This change in both color and constitution is due to the transposition of a hydrogen atom in the molecule from one group to another. Greenhalgh suggests that there may be a similarity between the phototropy of certain azo dyes on acetate group and the desmotropy of *p*-nitrosophenol. It is well known that acetate silk has a high affinity for amino groups, and, while nitrogen is usually considered rather inactive, the azo coupling undoubtedly has considerable activity. In the case of certain azo dyes on acetate silk, the position on connections of this azo group may possibly be so shifted or altered, by the presence or absence of light, as to cause phototropism.

"Phototropism is shown not only by the azo dyes on acetate silk, but also by some other nitrogen-containing groups, such as amino and nitro groups, and in certain cases under some conditions, it appears to be impossible to completely diazotize some amino compounds on acetate silk, which probably may be due to the highly affinity of this group for the acetate silk fiber. This certainly looks as though the chemical affinity of the acidic acetate silk fiber for the basic amino group of these dyes plays some part in dyeing this fiber," p. 123.

"In perfecting the series of dispersol dyes, the property of phototropism again came into prominence, as in the development of the ionamines; but the difficulty was again overcome satisfactorily. As before, the trouble was particularly prevalent on the greenish-yellow," p. 283.

"Early in the development of acetate silk it was well known that it absorbed a few dyes substantively, but these were mainly basics. Some of these dyes possess a fastness to light and washing on certain acetate silk which is rather unexpected and entirely out of relation to their fastness on other fibers, even without a mordant. However, the affinity, and therefore the fastness properties, of the various basic dyes, varies with the different brands of acetate silk. For instance, Lustron has the highest affinity for the basic dyes

of any known commercial textile fiber, while Celanese does not have such a high affinity for them. The difference is so great that with certain dyes under suitable conditions, the Celanese, as well as all other fibers, may be left practically unstained in a basic dye bath in the presence of Lustron. For example, if Lustron and Celanese are dyed together in the same bath with a basic dye, such as Rhodamine or Malachite Green, the Lustron will take on a very full shade while the Celanese will be dyed only a comparatively light shade.

"Very possibly the affinity of the acetate silks for the basic dyes is largely due to their sulfate and acetate groups and the difference in the affinity of the two varieties mentioned above may largely be due to the differences in their composition, although the finishing process may play some part in the difference. The fastness of the basic colors on acetate silk appears to follow closely the affinity of the basic dyestuff for the acetate silk and for this reason we may rightly expect the basic dyes on Lustron to have better fastness than on Celanese. Even with light fastness of many of the unmordanted basic dyes is unexpectedly good on Lustron," p. 137.

In the "sulfato dyes," the "alcoholic sulphuric acid group, $-C_2H_4SO_4H$, attached to nitrogen has a somewhat similar function to the sulfonic acid group in dyes. The resulting dye is therefore soluble; acid in character, and therefore suitable for dyeing real silk and wool. Apart from the fact that these properties are characteristic of these new dyes, their use is not restricted to the dyeing of animal fibers, as it was originally recognized that some of them would dye cotton from a neutral or alkaline dye bath, while others may be used in the manufacture of lakes and pigments. Members of this group suitable for use as mordant dyes were also prepared. Now it has been discovered that certain dyes of this class are suitable for acetate silk, so that it may be possible to dye almost any combination of fibers in certain colors with this one class of dyes," p. 198.

Some of the colors listed on p. 208 under Ciba dyes are a bit puzzling to the layman: bambino, cherub, pangoon, spice, electric, banner.

"In applying the developed colors to acetate silk it is advisable to use just the reverse of the usual method of applying them to cotton. In other words, instead of padding the fiber with the naphthol and then developing the color in a bath containing the diazotized base or amine, as on cotton, the acetate silk should first be treated with base or amine, and this diazotized on the fiber, either in the presence of the developing component, or before entering the developing bath. This is on account of the much greater affinity of the bases for this fiber, than that of the naphthols or phenols. If the process as used on cotton is attempted upon acetate silk, the shades are usually dull, the fastness poor, and the results generally unsatisfactory," p. 214.

"The fact that many compounds insoluble in water dye acetate silk, and that the usual method of solubilizing dyestuffs, that is by sulfonating, usually destroys the affinity of the product for acetate silk, led to research for a new method of solubilizing the insoluble bases, dyes, etc., without reducing their affinity for the acetate silk. Several methods of solubilizing without introducing the sulfonic group have been mentioned, such as the introduction of the carboxyl and other acidic groups, etc., but the Ionamines are entirely new products, quite different from those mentioned, and are applied by an entirely new method. They were the first products developed to meet the exacting requirements of the acetate silk dyeing industry and are today one of the most important groups of dyes for this purpose," p. 264.

"The dispersol type of dyestuffs or method of application, whichever we may care to call it, is the second entirely new group of dyestuffs to be developed especially for use upon acetate silk. . . . It is a heretofore unexpected fact, possibly not at all characteristic of dyeing acetate silk only, that certain compounds (dyestuffs) have a much greater affinity for acetate silk when in colloidal solution, possibly in even a rather coarse dispersion, than when they are in true solution. This is particularly the case where the compound is solubilized by means of chemical combination with some solubilizing reagent, such as the solubilization of certain bases by means of hydrochloric acid to form their hydrochlorides, or by sulfonation.

"When the dyestuff is solubilized by the chemical method, as the sulfonate or hydrochloride, it is a case of the fiber's chemical and physical affinity for the basic portion of the dyestuff against that of the acid radicle and the water. Where the physical method of solubilization is used, such as in the dispersol process, there is no acid radicle affinity present in the dye bath, and the solubility of the dyestuff in water is usually so low that the compound is on the point of actual precipitation. As the attraction in this case is practically all one way, that is towards the fiber (acetate silk), it is not surprising that deeper shades are obtained than by the older chemical methods of solubilization, where at best, the dyestuff only comes to equilibrium between the aqueous-acid phase and the non-aqueous fiber phase.

"Where the chemically solubilized dyestuff is highly hydrolyzed in the dye bath, as in the case of the Ionamines, we may expect the free basic portion of the hydrolyzed molecule to enter into either physical or, in this case, more probably chemical combination with the non-aqueous (fiber) phase, in which it appears to be more soluble than in water, and which is acidic in character, due to the acetate groups present. This in turn allows a further hydrolysis of the dyestuff, with a further absorption of free base, etc. Here there is probably an equilibrium reached between the aqueous acid phase and non-aqueous acid (fiber) phase, while with the physically solubilized dyestuff, there is more likely to be practically a complete exhaustion of the colloidal dyestuff up to the point of saturation of both the chemical and physical affinities of the fiber," p. 278.

"The fastness to light of many of the more or less light-fugitive colors on acetate silk may be very considerably improved by the presence of the fiber of certain colorless organic compounds of a basic nature, such as aniline, β-naphthylamine, benzidine, etc. Certain dialkylanilines, such as dimethylaniline, are particularly effective. These products are applied by the dispersol method, that is, they are dissolved in a dispersing agent, such as sulforicinoleic acid or Turkey-red oil, and this is either added to the dispersol dye bath, or applied in a subsequent bath.

"Apparently as much as about 2 per cent of the dialkylaniline is taken up by the silk, either in solid solution or chemical combination, due to its high affinity for such basic compounds. As much as 5 per cent of the product appears to have been used in some instances. Where it is all combined in the acetate silk fiber, there is no noticeable odor, but the odor of an excess may be detected. This would apparently indicate a chemical combination with the acetate silk of that portion taken up by the fiber. Their protective action is probably based upon their absorption of the ultraviolet rays as spectroscopic investigation shows that after this treatment, the acetate silk absorbs all light rays below about 3400 A. U. The dialkylanilines are readily prepared for use by the dispersol method by boiling them with about their own weight of Turkey-red oil. This solution is added directly to the aqueous bath," p. 310.

Wilder D. Bancroft

A Text-Book of Inorganic Chemistry. *By J. Newton Friend. Vol. IX. Part II. 23 × 16 cm; pp. xxv + 265. London and Philadelphia: Charles Griffin and Company; J. B. Lippincott Company, 1921. Price: $7.50.* This number deals with iron and its compounds. The chapters are entitled: the early history of iron; the mineralogy of iron; preparation and properties of pure iron; the corrosion of iron; general properties of iron salts; compounds of iron with hydrogen and the halogens; iron and the elements of Group VI; iron and the elements of Group V; iron and the elements of Groups IV and II; detection and estimation of iron.

"At the dawn of the human era man would seize upon any stones, branches, or any hard materials lying at hand for purposes of offence, defence, or the chase. Later on it would occur to him to improve upon the natural shapes by chipping, and he would soon discover that flint is particularly amenable to such treatment. Thus would originate the flint weapons and tools which have been discovered in large quantities in modern times, and which antiquaries have made use of to throw interesting light upon the manner in which primitive man lived during what has been aptly termed the *Stone Age*.

"In all probability during his search for suitable stones early man occasionally stumbled across meteoric iron. Finding that it did not crack on being hammered, that it possessed great tenacity and admitted of being rubbed to a fine, hard edge, he would prepare from it his most valued weapons.

"This does not constitute the beginning of what antiquaries term the *Iron Age*, for man at this period did not recognize any relationship between metallic iron and the red or brown earthy haematites around him. He regarded the iron merely as a particularly useful but unfortunately rare kind of stone, and not as a substance that he could manufacture for himself," p. 1.

"Ages elapsed before man discovered that certain "stones," on being heated in a fire, yielded a new "stone" capable of being hammered into useful shapes, and differing from the original stone in most of its other properties. This new product is now called copper or bronze, according to its composition. At first, no doubt, it was a matter of accident whether bronze or copper was produced. In districts such as Cornwall, where copper and tin ores occur in association, they would be reduced together as one and the same, yielding what may be termed a "natural bronze." In Hungary, where copper ores are associated with those of antimony, early implements consist of an alloy of copper containing up to 4.5 per cent. of antimony. Similarly Egyptian implements contain arsenic, whilst those from Germany contain nickel.

"The discovery that bronze is not obtained from a single ore but from a mixture of at least two ores represents a high standard of metallurgical knowledge, soon to be followed, if not indeed already preceded by the discovery of iron. The question now arises as to how many years iron—whether native, meteoric, or manufactured—has been known to and used by different peoples. Just as the nations to-day differ in the relative degrees of their civilisations, so in past ages some of the peoples were living in their stone age whilst others were using implements of bronze and yet others had become familiar with iron. Thus Britain was passing through her stone period at a time when iron was already known in Assyria, in Egypt, and probably also in China. Again, at the time of the Roman invasion of Britain the southern tribes used bronze implements and were familiar with iron, whilst the northern tribe of Brigantes was still in their stone age. Iron was known in Egypt at least some 3500 B. C., although it did not come into common use probably until the fifth or sixth century B. C. Possibly the iron found its way thither from Ethiopia, where iron smelting was probably practised at an earlier date than in Egypt. During blasting operations within the Great Pyramid at Gizeh in 1837, an iron tool was found, which, if coeval with the pyramid, proves that iron was known in Egypt at the time of the Fourth Dynasty—that is, some 5500 years ago," p. 2.

"The problem of the origin of the haematites has been the subject of much discussion. The view is largely held that, in the instance of Cumberland and Lancashire, the haematite has gradually replaced the calcium carbonate, molecule by molecule. This is supported by the fact that the ore and rock appear to have "grown together," as the miners express it, the ore gradually passing into the limestone and possessing precisely similar stratifications and dip. Again, casts of mollusca and other fossils characteristic of carboniferous limestone have been found in the haematite, as well as crystals of haematite pseudomorphic with calcite. It does not follow, however, that all haematites are necessarily formed in this way; local conditions must always be taken into consideration. Admitting for the sake of argument the foregoing or metasomatic origin of the north-country haematites, the next point of interest is to determine how this molecular substitution could have taken place. The formation of anhydrous ferric oxide would appear to postulate an application of heat in some way or other, and volcanic activity seems to be the most easy way by which such heat might be forthcoming. It seems possible, therefore, that the carboniferous strata were overlain by ferruginous Permian and Triassic deposits. Waters, charged with ferrous iron in solution by passage through these deposits, percolated through the limestone beneath dissolving out the calcium carbonate and leaving ferrous carbonate. This slowly oxidized, and under the influence of heat yielded anhydrous ferric oxide.

"Red haematite has been found at Torquay, apparently pseudomorphic with pyrites, which is remarkable, for, although pyrites is frequently oxidised to limonite, it is indeed rarely that it is converted into anhydrous haematite. It is suggested that pyrites was converted into ferric chloride by the action of sea water, and that this reacted with limestone to yield anhydrous ferric oxide in some such manner as that indicated above," p. 17.

"Closely connected with the power to occlude gases is the property of transfusion, by virtue of which gases are able to pass through iron. In 1863 Cailletet showed that nascent hydrogen could pass through an iron vessel immersed in sulphuric acid at the ordinary temperature, and this has been confirmed by numerous later investigators. This diffusion of nascent hydrogen is not inhibited even by a pressure of 14 atmospheres. Molecular hydrogen only passes through iron at a measurable velocity when the temperature is raised. Below 325°C the velocity is inappreciable, at 350°C. it becomes perceptible, and at 850°C. the velocity is some forty times as great," p. 46.

"When heated in air or oxygen a piece of polished iron undergoes no apparent change below a temperature of about 150°C. Further heating results in tarnishing. As this is merely slight superficial oxidation, the temperature at which it becomes distinctly visible depends upon the duration of the experiment. Thus, for example, prolonged heating at 170°C. may result in the production of a pale straw colour, although for short periods of time a temperature of 220°C. is normally required to produce the same effect. Given reasonably uniform conditions, however, the extent of the exidation, which may be judged by the characteristic hues imparted to the iron, is a fairly accurate indication of the temperature. Workmen avail themselves of this with remarkable skill in tempering steels," p. 47. Curiously enough, the author does not make the definite statement that these are thin-film colors.

There is a very fair discussion of passivity of iron on pp. 55-60; but the author commits himself only to the statement that "the probability is that several kinds of passivity exist and that not a few of the different theories are correct in certain cases." While this is very likely so, it is of no use unless the author points out where the oxide theory, for instance, breaks down—and he does not do this—or what theory holds in what case and why.

Under corrosion of iron, p. 67, the author says that "the fact thus established that the presence of liquid water is essential to corrosion points to the conclusion that before iron can rust it must pass into solution, presumably first in the ferrous state, from which it is then precipitated by atmospheric oxygen in the form of hydrated ferric oxide or rust. In other words, the reaction is essentially ionic." The author would have said electrolytic instead of ionic if he had chosen his words carefully.

"Methyl, ethyl, and propyl alcohols are oxidised by permanganate or hydrogen peroxide in the presence of ferrous salts. If ferrous sulphate is employed, the ethyl alcohol is, in dilute solution, oxidised by the permanganate to aldehyde; but in the presence of ferrous oxalate the oxidation proceeds further, acetic acid resulting. Thus

$$CH_3 . CH_2OH \longrightarrow CH_3 . CHO \longrightarrow CH_3 . COOH.$$

These reactions proceed so regularly that they may be followed up quantitatively. Ferric salts have no catalytic influence upon these reactions. Iron salts, however, can act as oxygen-carriers in the absence of such powerful oxidisers as hydrogen peroxide and potassium permanganate. Thus, for example, it is well known that, upon exposure to sunlight, iodine is ordinarily liberated from a solution of mercuric iodide in potassium iodide. Curiously enough, if traces of iron salts are rigidly excluded, the liberation of iodine does not take place," p. 80.

"The aerial oxidation of solutions of ferrous salts may be accelerated by certain micro-organisms, known as iron bacteria. Mumford describes an organism through the agency of which a dilute solution of ferrous ammonium sulphate was completely oxidised to ferric hydroxide in fewer than thirty-six hours at 37°C., no iron remaining in solution. There can be no doubt that the natural deposits of bog iron ore, occurring in Sweden and elsewhere, owe their existence to the action of these lowly organisms," p. 81.

The reduction of ferric salts by thiosulphates, according to the equation $2Fe^{\cdots} + 2\ S_2O_3'' = 2Fe^{\cdot\cdot} + S_4O_6''$, is said to rank as one of the few tetramolecular reactions that have been studied, p. 84.

"An interesting lecture experiment to illustrate suppression of hydrolysis of ferric chloride under certain conditions consists in diluting a solution of the salt until it is practically colourless. Concentrated hydrochloric acid is now added, and the solution assumes a yellow colour, characteristic of the un-ionised $FeCl_3$-molecule. The addition of glycerol to a solution likewise intensifies the colour, and this is attributed to diminished dissociation consequent upon the introduction of a substance possessing a lower dielectric constant," p. 100.

It is misleading to say, p. 128, that Foote and Saxton found that the amount of water chemically combined with precipitated ferric hydroxide corresponds to the formula $Fe_2O_3 . 4.25H_2O$. This refers to adsorbed water and not to water combined according to the law of definite and multiple proportions.

"The action of hydrogen peroxide on ferrous chloride, ferrous or ferric hydroxide, or ferric chloride results in the formation of a pale red substance which is very unstable—so much so that its composition cannot be established with certainty," p. 130.

"The pores in a copper ferrocyanide membrane are exceedingly fine, ranging from 8 to 60 $\mu\mu$ in diameter, the average being from 15 to 20 $\mu\mu$. The osmotic action is not due to a selective mechanical filtration, but to selective adsorption on the surface of the membrane. Hence such membranes as have the smallest pores and expose the greatest superficial area are the most efficient semipermeable structures," p. 209. It is not stated what is adsorbed selectively by the membrane. It would have been shorter to have said negative adsorption instead of selective adsorption and we should not now be wondering whether the author does or does not understand the theory of semipermeable membranes.

Wilder D. Bancroft.

Equilibria in Saturated Salt Solutions. *By W. C. Blasdale. 23 × 16 cm; pp. 193. New York: Chemical Catalog Company, 1927. Price: $4.50.* In the preface the author says: "The widespread interest in both practical and theoretical chemistry, which was one of the results of the Great War, has given rise to a demand for brief treatises dealing with a number of the special fields of chemical science. Of these the nature of the heterogeneous equilibria which exist in systems composed of water and one or more electrolytes is of major importance. Although many of the technical processes in general use employ separations which involve such equilibria, the available information relating to such processes is often purely empirical and fragmentary, whereas an adequate understanding of the possibilities of such processes under varying conditions clearly calls for a general and comprehensive treatment. It is one of the chief objects of this volume to show how a general treatment can be applied to the class of systems under consideration, the method employed being to discuss in turn a series of typical illustrations of such processes for which fairly complete data are available. Aside from its technical application, this subject is of interest from a purely theoretical point of view and furnishes one of the many striking illustrations of the results obtained by the application of thermodynamics and the modern conception of the nature of chemical forces, only those features of these theories which are essential have been made use of."

The chapters are entitled: water as a typical one-component system; systems composed of water and a single salt which does not form hydrates; systems derived from water and a single salt which forms one or more hydrates; systems composed of water and two electrolytes which yield a common ion but do not form solid solutions; three-component systems derived from water and two electrolytes which yield a common ion and which form mixed crystals; systems derived from water and two electrolytes which yield one hydrogen ion, or one hydroxyl ion, or both, four-component systems derived from water and three electrolytes which yield a common ion; systems derived from water and two electrolytes which do not yield a common ion; quinary or five-components systems derived from water and three or more electrolytes; six-component systems.

It is very difficult to treat a subject like this in an interesting way and the author has not escaped the common failing. The general presentation is quite satisfactory, though one might take exception to the so-called thermodynamic treatment. To the author thermodynamics apparently means fugacity; but that is probably a necessary consequence of his thermodynamic environment. He makes no reference to Gibbsian surfaces although Freeth seems to consider them as absolutely essential.

The reviewer was distinctly interested in the following paragraphs. "Changes in the degree of hydration of a salt are invariably associated with prominent changes in the crystalline form it assumes as well as in its physical properties including its ability to dissolve other salts. There are no convincing illustrations of solid solutions whose component salts are both hydrated but hydrated differently. It is true that the percentages of water found in some of these solids differ slightly from those required for equal hydration, but it is customary to attribute these discrepancies to occlusion of the mother liquor from which they separated. In general unless the two salts are capable of existing in the same degree of hydration over a similar range of temperatures, and unless the two hydrates possess similar crystallographic properties, a continuous series of solid solutions is not possible. There are however many examples of solid solutions composed of a hydrated and an anhydrous salt. The systems $(NH_4)Cl - FeCl_2 - H_2O$, $(NH_4)Cl - NiCl_2 - H_2O$ and $(NH_4)Cl - MnCl_2 - H_7O$ might be cited," p. 100.

"It was suggested by Ostwald, as a result of qualitative experiments on the process of crystallization, that solutions may contain two degrees of supersaturation, a metastable range within which inoculation of the solution with crystals of appreciable size causes a slow growth upon the added crystals, and a labile range within which crystal nuclei are formed spontaneously, either with or without mechanical agitation only. The actual position of a curve on the concentration-temperature diagram, which separates these fields was determined by Meyer and Isaacs for a number of inorganic salts, by Hartley and Thomas for a number of organic compounds and by Hartley, Jones and Hutchinson, who studied the system $Na_2SO_4 - H_2O$ with great care. Some of their results are represented in Figure 14 which shows a clearly defined supersaturation curve for ice along AB and for $Na_2SO_4 . 7H_2O$ along BC, both roughly parallel to the normal solubility curves. They were not able to locate a corresponding curve for Na_2SO_4 from 55° to 95°. Although acceptance of this proposal of Ostwald has been very limited the theoretical explanation offered by Hartley and Thomas seems satisfactory. It is based upon the well-established fact that, owing to surface tension phenomena, the solubility of a crystal increases as its size decreases and therefore that metastable supersaturation represents supersaturation with respect to crystals of easily recognizable dimensions only," p. 65.

"A solution containing 83.5 percent of zinc chloride when saturated at 68° could be cooled to zero without crystallization. Such solutions were very viscous and became glassy at −70°," p. 62.

"The diagram clearly requires that if carnallite be added to water, solid KCl will be the first solid to separate, and a large percentage of the KCl in this mineral can be obtained in pure form by simply adding water and evaporating. Still greater yields can be obtained by working at higher temperatures," p. 83.

While the statements in the preceding paragraph are correct, it would seem more economical, to leach out the magnesium chloride than to dissolve the carnallite and evaporate the water, unless there is some impurity present which is not mentioned. What they actually do is to leach with a magnesium chloride solution in which only carnallite dissolves. The preparation of ammonium nitrate during the war was such a triumph for phase rule methods that it is disappointing not to find any reference to it. While accurate details may not be available, it seems probable that the author could have obtained from Freeth all the data necessary for a book of this sort.

The mispelling of Abegg, Clibbens, and Stortenbeker is probably due to the author; but the horrible misuse of capital letters on pp. 11-13 and elsewhere is undoubtedly the fault of the publishers. It should never happen again. These pages are an eye-sore.

Wilder D. Bancroft

Volume Alterations on and in Solution. *By Frank L. Teed. 19 × 12 cm; pp. x + 62. London: H. K. Lewis and Co., 1926. Price: 3 shillings 6 pence.* "This paper divides itself into three sections: 1. A method for ascertaining the volumes of the constituents of a mixture, after mixture. 2. A method for ascertaining the rate of expansion by heat of the constituents of a mixture, after mixture. 3. A suggested working hypothesis to explain certain abnormal specific heats of alcohol mixtures." p. vii.

The second and third sections of the paper do not seem especially important but the method elaborated in the first section is an interesting and readily applied approximation. The method proposed is stated as follows:

"In 100 volumes of a mixture of A volumes of one substance and B volumes of another substance where the sum of A and B is not equal to 100, there must be some factor a by which A is expanded or contracted, and another factor b by which B is contracted or expanded. This can be put in the form of an equation: $Aa + Bb = 100$

"This being a simple equation with two unknowns, is, in the language of Algebra, indeterminate. If we now take 100 volumes of a mixture of the same two substances, slightly varying the proportions, we get another equation: $A'a' + B'b' = 100$ where A′ and B′ are the new volumes of the two substances before mixture which are contained in 100 volumes of the mixture, and where a' and b' are the new factors. . . .

"No great error would be committed when A is very near A′, and consequently B very near B′ if we assume provisionally that $a = a'$ and $b = b'$, and that the results for a and b apply to a mixture half way between A + B and A′ + B′." p. 2.

The author then proceeds to show algebraically that the error thus introduced is slight and is probably within the experimental error of the specific gravities on which the calculations are based. He is apparently justified in this for in the applications he deals with concentrations differing by only one or two percent.

Professor Bancroft has pointed out, however, that such calculations may be made accurately by plotting the volume of the solution containing a fixed amount of component B against the grams of component A added. The first derivative of the equation representing such a curve will be dV/dg and will be equivalent to the increase in volume of an infinite amount of solution when one gram of component A is added. This is equivalent to a of Teed's method which he assumes to be the same for the reference concentrations and for the calculated concentration half-way between them. It is evident that the tangents at these three points on the curve so plotted will be parallel only if the curve be a straight line or a line of constant curvature over the region in question. It is only under these limitations that the equations of Teed are truly simultaneous and the method strictly valid.

Extensive tables show values of a and b calculated for mixtures of ethyl alcohol-water, methyl alcohol-water, acetic acid-water, sulphuric acid-water and sugar-water. It is shown that on mixing various alcoholic solutions in water of different strengths with an equal bulk of water, there is first expansion for the dilute solutions, but, when the resultant mixture exceeds 20 percent alcohol, the volume of the solution is less than the sum of the volumes of the original components. The same phenomenon is observed with acetic acid and with methyl alcohol and water.

It is a bit disappointing to find no attempt to explain what really causes the calculated contraction or expansion or what changes in the molecular complexity of the substances these volume changes may indicate. Possibly the method of approach presented in this book may aid in the solution of this important question.

Herbert L. Davis

A METHOD FOR COMPARING THE TIMES OF MIXING OF TWO TRANSPARENT LIQUIDS IN DIFFERENT PROPORTIONS, AND SOME EXPERIMENTAL RESULTS, PARTICULARLY WITH GASOLINE AND CARBON BISULPHIDE[1]

BY L. E. DODD

Introduction

The purpose of this article is to describe an optical method for determining the "time of mixing" of two transparent liquids, not too readily miscible, and to record some experimental results. The degree of reproducibility attained appears to justify further work with the method, which is a particular adaptation of the more general "method of striae." The "Schlierenmethode" of Toepler,[2] the aberrational effect on the rays of light passing through a glass lens[3] because of the striae in it, particularly of a certain general type,[4] that in some cases results in a blurring of the image, and the unsteadiness, or "boiling," of a telescopic image due to turbulence of the atmosphere, which consists of motion of atmospheric striae that in turn are due to varying density in the air between the object and the telescope [5]are all well known.

In general, striae are physical inhomogeneities of a given medium, which must be transparent for their study by an optical method such as that described here, and they are accompanied by corresponding variations in the optical density, so that the refractive index changes from point to point. Their presence can be detected by the scattering effect upon a beam of light transmitted through the medium. The more pronounced striae are easily seen by simply looking into the transparent medium when it is illuminated in a suitable direction by ordinary daylight. A common example of striae in air is that of the visible so-called "heat" rising from a hot surface. The mass of striae in this case is formed of air heated unevenly. Often the index variation is narrowly localized, as in much optical glass that is still usable. In such cases the striae appear as threads or sheets of transparent material, imbedded in a medium that otherwise has a uniform refractive index.

Striae are rendered visible in any one of three different ways: (1) the medium in which they occur may be viewed directly, as mentioned above, the direction of view being generally toward the source of illumination when the latter is not too bright; (2) a real image of the medium, or, more exactly, of a

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[1] This article includes the material of a paper presented before the American Physical Society, Pacific Coast Section, at the Pasadena meeting, September 18 (1923), abstract of which appeared in the Physical Review, **22**, 527 (1923).

[2] Toepler: Pogg. Ann., **131**, 33 (1867); see also R. W. Wood: "Physical Optics."

[3] U. S. Bureau of Standards Scientific Paper, **373** (1920), "Characteristics of Striae in Optical Glass," by Smith, Bennett, and Merritt.

[4] U. S. Bureau of Standards Scientific Paper, **333** (1919). "Striae in Optical Glass," by A. A. Michelson.

[5] See discussion of scintillation in Wood's "Physical Optics."

definite sheet, or plane, of it perpendicular to the axis of the rays, may be projected to a screen, where the striae appear in the image; or, (3) by simple means,[1] "refraction shadows" of the striae may be made to appear on a suitable screen, preferably translucent, held in the path of the light. For highest visibility, all three methods employ a source of light as concentrated as possible, in order that the aberrations, caused by the striae, in numerous pencils of rays of light from the many different points in an extended source, may not overlap and produce a field of quite uniform intensity, in spite of the presence of the striae, in this way masking them.

The type of striae occurring where one liquid has been added to another, and which persists until the "mixing," as the term is defined in this article, has been completed, is common. The particular method to be described makes possible a particular definition of "mixing" that is stated in fairly specific experimental terms. Two liquids are here regarded as "mixed" when the striae have disappeared, as judged by the clearing up of a real image formed by rays that have traversed the liquid mixture. The precision of such a method is raised by the use of a long focus lens. The relatively rapid final clearing up of the image gives approximately the time at which the mixing is completed according to the definition. The "time of mixing," that is, the elapsed time which under the given experimental conditions is necessary for the clearing up of the image, depends among other factors upon the method of determining the "instant of start" of the mixing, or time zero. This requires a separate definition, one that is based likewise on the experimental conditions, and is likewise fairly precise. It will be stated later in the article, following a description of the apparatus.

The "time of mixing" depends on a number of factors, including the particular liquids used, and the "rate of stir," which in turn is affected by the particular design of the stirrer, its size, shape, and amplitude of motion relative to the shape and size of the vessel and the total volume of liquid in it, the location of the stirrer in the vessel, and the nature and rate of its motion. A temperature effect is to be expected, but none was established in the present work, which was all done at the approximately constant temperature of the room.

Apparatus and Method of Stir

Optical System. Fig. 1, with legend, shows the scheme of the optical system as viewed from above. The length of the path of the rays from the objective, *e*, to the translucent screen, *g*, was approximately 15 ft.

Tank. The mixing vessel, *d*, was a commercial rectangular battery jar, of outside dimensions $2 \times 2\frac{1}{2} \times 4$ inches. The inside dimensions of the horizontal section were about 4×6 cms. The two parallel walls of larger area, used as windows of the tank, were ground and polished plane on the outside, being left from 3 to 3.5 mms. thick. No attempt was made to modify the inside surfaces, which were not precisely flat, although smooth, as the vessel was blown in a mold during manufacture. However, the aberrational effect

[1] L. E. Dodd: J. Am. Ceramic Soc., 2, 977 (1919).

upon the transmitted light, due to departure from flatness on the interior, was lessened because of the relatively low index between the glass and the contained liquid. No greater flatness could be claimed for the tank floor than for the inside walls. None of the inside corners were sharply angular. For the present use the vessel was provided with a ground plate-glass cover fitting tightly on the upper, open end, whose edges were likewise ground flat. The cover had a 4-mm. hole drilled in it to permit the handle of the stirrer to project upward out of the tank.

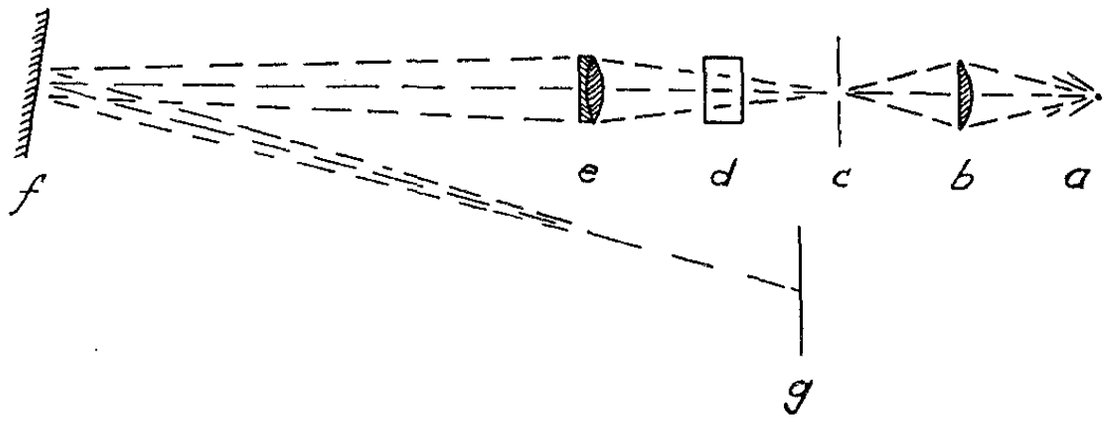


FIG. 1
Optical System for determining the Time of Mixing of Transparent Liquids by Method of Striae.

a, 100 w. Mazda
b, condenser lens
c, opaque screen with 2 mm. aperture
d, glass mixing tank
e, objective, f = 30 inches
f, plane, plate glass mirror
g, translucent screen to receive real image of aperture at c.

Stirrer. A metal meshwork stirrer combined simplicity of construction and operation with thoroughness in its stirring effect. It consisted of a rectangular loop of iron wire, about 2.5 mms. diameter, bent sharply at the corners and soldered so as to form a rigid frame. The loop was 3 × 5 cms. in size, and had a sheet of galvanized wire cloth (ordinary fly screen) fastened rigidly to it below by local soldering, to give it the motion of the loop itself. The sheet of metal screen was about the same size as the loop; its edges did not project much beyond the loop toward the glass wall. There were fourteen squares of the mesh-work in each linear inch of the screen, including the wires, which were about 0.3 mm. diam. The vertical handle, also of the same size of iron wire, was attached rigidly by solder at one corner of the loop, and extended perpendicularly to its plane, passing out through the tank cover as already mentioned. Thus the plane of the loop, covered with its metal network, remained approximately horizontal. The free end of the handle was filed to a hook shape, to receive a fine piano wire suspension.

Motion of the Stirrer. The suspension wire was in turn hung from the end of a hardwood lever about 2.5 ft. long, mounted on a horizontal axle so that it formed a walking beam. The outer end of the lever was jointed to the

iron rod of a reciprocating system operated by a small D. C. motor. The vertical motion of the stirrer suspension could be regarded as very nearly simple harmonic. The plane of the meshwork itself had very little angular motion. Adjustments were such that when the fine wire suspension was at the upper end of the lever stroke, the meshwork was lifted clear of the free surface of the liquid by about $\frac{1}{4}$ inch, and with the suspension at its lower position, the meshwork rested momentarily on the bottom of the tank with slack in the suspension wire. This slack amounted to about $\frac{1}{4}$ inch also, so that the motion of the stirrer in the liquid was symmetrical in character.

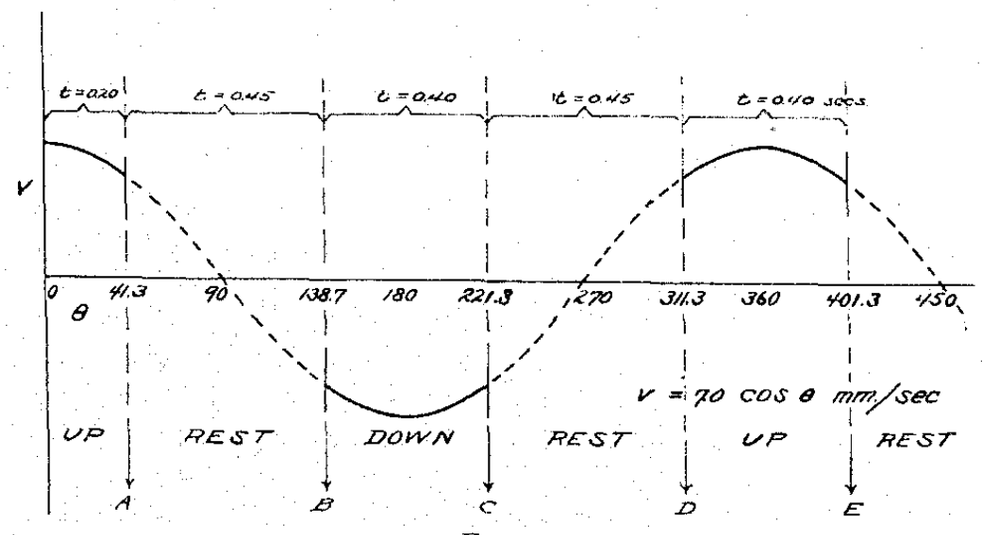


FIG. 2
Approximate Motion of the Stirrer

Fig. 2 gives a cosine curve of velocity that holds for true simple harmonic motion. It is taken to represent approximately the actual motion of the stirrer. The parts of the curve, each including a crest or a trough, drawn in as continuous lines, correspond to time intervals when the stirrer is in motion in the liquid, and the parts drawn in as dashed lines correspond to the intervals when the stirrer is, in effect, at rest relative to the liquid, that is, when it is either out of the liquid, or at rest on the tank floor. At the points A and E the stirrer emerges from the liquid into the air. At point B it reenters the liquid, at C it stops abruptly on the tank floor, and at D it starts abruptly upward through the liquid. In the present work the period of the stirrer could be kept approximately constant at about 1.7 secs., as tested with stopclock, by maintaining constant voltage on the motor. The performance of the stirrer is shown in Table I. The presence of the liquid in the tank had little or no effect on the period.

The constant total volume of liquid used, 60 cc., gave an approximate depth of liquid in the tank of 25 mms. The double amplitude of the end of the wooden lever at the point where the suspension wire was attached, was 38 mms. Assuming that the meshwork was precisely at the center of the liquid vertically when the suspension was at its oscillation center, the velocity of the meshwork at that instant was 7.0 cms./sec., with the amplitude of the suspension taken at 19 mms. and the period at 1.7 secs. The actual

period may be regarded as within 5% of this figure, which will serve the purpose of discussion. The harmonic velocity increased from 5.2 at the tank floor to 7.0 cms./sec. at the center of the liquid, and then decreased to 5.2 cms./sec. upon emergence from the liquid. The same succession of velocity values at the same places was repeated during the down stroke. Thus the

TABLE I

Performance of the Stirrer

Date (1923)	No. of Cycles	Time (secs)	T	Remarks
Aug. 15	40	67.5	1.69	Period of stirrer suspension without stirrer.
" "	40	67.0	1.68	Period of suspension with stirrer attached and moving in air.
" "	40	66.8	1.67	" " " "
" "	40	66.8	1.67	Period of suspension with stirrer attached and moving in 60 cc. gasoline in tank.
" "	40	66.8	1.67	Same, but stirrer moving in 60 cc. CS_2 in tank.
" "	40	66.8	1.67	Stirrer moving in air.
Aug. 16	40	66.5	1.66	
Sept. 3	10	16.4	1.64	End of series 6.
" "	10	16.2	1.62	End of Series 7.
Sept. 4	10	16.6	1.66	
Sept. 5	10	17.4	1.74	
Sept. 11	20	35.4	1.77	Series 10 started this date. Voltmeter and rheostat control on motor. The seven readings were taken successively.
" "	20	35.2	1.76	
" "	20	36.2	1.81	
" "	20	35.6	1.78	
" "	20	35.4	1.77	
" "	20	35.6	1.78	
" "	20	35.4	1.77	
Sept. 12	20	35.0	1.75	During Series 10.

stirrer was alternately in motion in the liquid and then, in effect, at rest relative to it. The manner of coming to rest on the tank floor was different to be sure from the effective coming to rest as the stirrer broke through the surface and was lifted clear of the liquid. The "rest" intervals were slightly longer than the motion intervals, being 0.45 and 0.40 secs. respectively. During the periodic "rest" intervals of the stirrer the inertia of the currents set up by its passage through the liquid maintained in considerable degree the process of stirring, so that it was in a sense continuous. The precise quantitative effect on the mixing, of the periodic pause in the motion of the meshwork stirrer, would be interesting to know. That it lengthens the mixing time is probable, and this circumstance should contribute to relatively low errors and to consistency in results by increasing the magnitudes to be measured. The

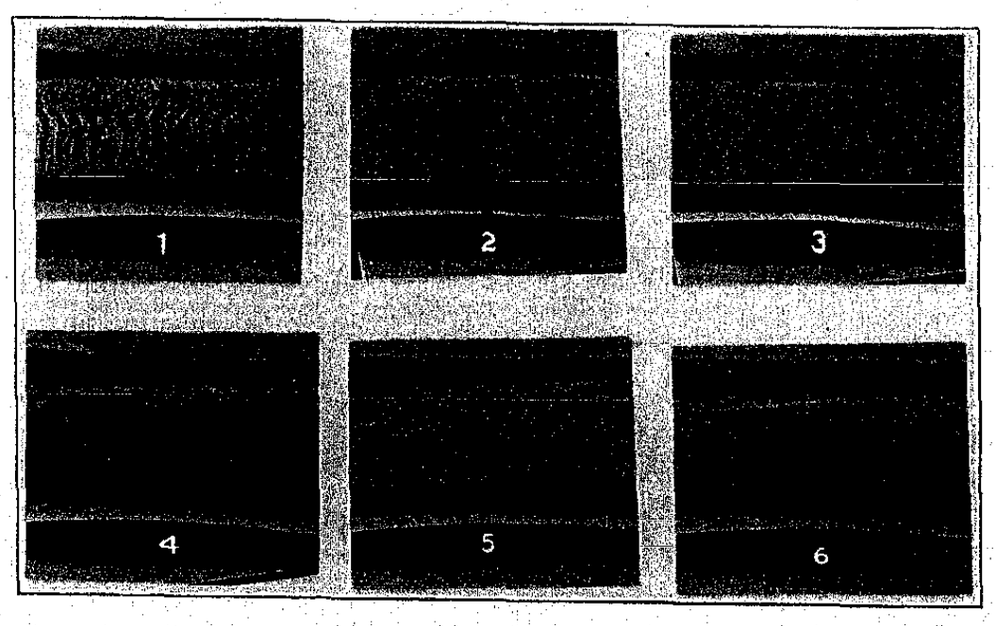


FIG. 3
Periodic Shadowgraphs of the Striae during mixing, showing the Character of the Mechanical Agitation

distribution of the turbulence was quite uniform throughout the whole body of liquid, as indicated by the snapshot "shadowgraphs" ("refraction shadows" by short range projection) of Fig. 3. These six snapshots, taken successively at equal and relatively long time intervals, were made in some preliminary work where measuring by photography the time of mixing, was being considered.

In each of the six snapshots the meshwork stirrer is seen edgewise at an instantaneous position near the floor of the tank. The striae in the glass floor, where the rays of light traversed it edgewise, and reached the film, are seen at the bottom of the prints. Particularly in nos. 3, 4, 5, 6, refraction shadows of a different character are noted in the vicinity of the free surface. Those below the surface are probably due to a temperature effect caused possibly by slight evaporation at the surface, or by the entrance of the meshwork into the liquid, because of a slightly lowered temperature of the metal due to evaporation from it while in the air, even with the ground glass cover in

position on the tank. Temperature change may have contributed to, or even been chiefly responsible for, the refraction shadows above the surface, although the mere presence of some liquid flowing down the glass because of waves, might account for them. However, for the results presented in this article a greater volume of liquid was used, and these effects in the neighborhood of the surface did not themselves disturb the beam of light.

Start of Stir. Because of the relatively high speed of the motor, since reduction gearing was employed, and its quick response to the current, the "instant of start" was taken as that of closing the switch, with the stirrer, attached to the suspension wire, resting initially on the tank floor. An alternative method was to have the motor already running, but the loop of the suspension wire unhooked from the stirrer handle, and then suddenly to engage the hook with the loop, at the same time starting the stopclock. The method of closing the switch was chosen as being the simpler. In accepting this definition of the "time of start" the effect of the "initial stir" (see discussion below) is neglected.

Initial Stir. By this term is meant the stirring that results from adding the second liquid to that already in the tank without any motion of the stirrer itself. The amount of this initial agitation can be lessened, even to a negligible degree, as is evident from the present results, at any rate up to fully 50% gasoline, by permitting the liquid being added to flow into the tank slowly and gently. This lengthens the time before the stirrer is set into motion, giving diffusion or possible "chemical" action a longer time in which to act, but there seemed to be no marked effect attributable to these, at any rate up to 50% on the axis of abscissae. Further reference to the initial stir will be made in the discussion of results.

Appearance of Image. The presence of the striae, even when their structure had become fine through stirring, was indirectly known, either from low "definition" in the image, or from "boiling" of the image, or from both effects. When the image became "clear" and steady the striae were regarded to have disappeared, to the degree of precision attained in the present experimental setup.

Due to the aberrational (prismatic) effects in the tank, caused by lack of planeness, and absence of strict parallelism, of the inside wall surfaces, the image of the illuminated circular aperture serving as object was not itself circular, but usually roughly triangular in shape. In size it was an inch or more across. For the reason that the mean index of the mixture varied with the proportions of the two liquids, the dimensions of the image changed somewhat. In the region above 90% gasoline the shape of the image had materially changed to that of an oblong field, the colors not being so pronounced. This circumstance may have contributed to a somewhat erratic tendency shown by curve 10, Fig. 6, in this region, because of possibly less precise determination of the completion of the mixing.

The image may be described roughly as a color field with a darker central portion. But the color and the edges of the image were well defined. Any

"boiling" of the image, even local, due to moving striae in the tank, was plainly seen, perhaps as easily as if the image had been perfect. Throwing the image slightly out of focus appeared to accentuate a little the boiling effect, due possibly to the striae themselves approaching a focus.

Procedure

After the first of the two liquids had been poured into the tank, the stirrer was immersed so that it rested on the tank floor, with the ground glass cover in position, but rotated sufficiently in its own plane about the stirrer handle to leave an opening for the adding of the second liquid, after which the cover was moved to the closed position. The hook on the stirrer handle was next engaged in the loop of the suspension wire, and the stirrer started by closing the motor switch, as already mentioned. The stopclock was tripped when the real image cleared up with considerable abruptness. Room temperature, recorded in the data, was read from a standardized thermometer kept within a foot of the tank and on a level with it. There were no appreciable air currents about the apparatus.

Experimental Results

Ten series of readings altogether (Tables II to XII) were taken in August and September, and curves for five of them, viz., 1, 2, 3, 9, 10, are presented. Series 3 was an incidental test with distilled water and concentrated common salt solution as the two liquids mixed. The remaining series, 4, 5, 6, 7, 8, were tests for reproducibility. Series 4, 5, 6, were taken successively on the same day, series 8 and 9 successively on the following day. The continuous time intervals during which the readings of the ten series were obtained, and other information of a general nature, are given in Table XII.[1] For series 10, however, the actual time consumed by the readings was $19\frac{1}{2}$ hours in four separate continuous time intervals as follows: 1st day, 2 hrs.; 2nd, $5\frac{3}{4}$; 3rd, $4\frac{1}{2}$; 4th day, $7\frac{1}{4}$ hrs. (September). Each of the total of 248 readings recorded here, required an experimental "run" lasting anywhere from 18 secs. to $6\frac{1}{2}$ mins. In the nine series, excepting series 3, the two liquids were gasoline and carbon bisulphide, both commercial. The gasoline used, while not all from the same purchase, was obtained from the same filling station, the gravity being given at 62. The CS_2 was bought in different lots from different firms. For series 1 it was supplied by what will be called the "A_1" firm, and was found to be labelled "CS_2 97%, S 3%"; for series 2 it was obtained from the "A_2" firm, specimen labelled "CS_2 97%, S .3%," probably from the same manufacturer as before; series 4 to 9 inclusive, from the "A_3" firm, specimen labelled "97 to 99% pure"; series 9 and 10 from the "A_1" firm, specimen labelled "CS_2 97%."

Since the present work was regarded as the test of a method rather than the accumulating of an extensive mass of data for physico-chemical interpretation, little attention was given to purity of materials. This question should

[1] In Table XII, the X symbol appearing in the fifth and sixth columns indicates definitely the order in which the liquids were put into the tank, for the particular cases concerned.

not affect very appreciably conclusions that have been reached in this article, regarding the method in its present state of development. Each of the ten cases is treated as a mixing of two different liquids, say A and B. Liquid A and liquid B are each regarded as sufficiently similar in the nine cases to permit comparison of cases.

TABLE II

Series 1

Rdg. No.	% G	t (secs.)	Room Temp. (°C)	Rdg. No.	% G	t (secs.)	Room Temp. (°C)
1	1.7	20.3	22.2	6	83.5	71.7	
2	3.3	33.6		7	91.8	92.5	
3	8.3	54.3		8	95.0	108.5	
4	16.7	92.0		9	96.3	87.5	
5	50.0	85.3		10	98.0	80.8	22.2

TABLE III

Series 2

Rdg. No.	% G	t (secs.)	Room Temp. (°C.)	Rdg. No.	% G	t (secs.)	Room Temp (°C.)
1	0.8	18.5		14	66.7	210.2	
2	1.7	36.0		15	75.0	240.0	
3	3.3	30.0		16	83.0	245.0	
4	5.0	32.5	23.2	17	85.0	345.5	
5	18.3	63.5		18	86.8	367.0	
6	10.0	57.3		19	88.5	336.2	
7	13.3	75.2		20	90.0	316.5	23.2
8	16.6	108.2		21	91.5	358.5	
9	25.0	132.8	23.2	22	93.6	309.2	
10	33.1	178.5		23	95.0	243.8	
11	41.5	221.3		24	96.5	174.2	
12	50.0	272.0	23.2	25	98.0	157.8	
13	58.5	272.1		26	98.8	133.0	23.1

TABLE IV

Series 3

Rdg. No.	% G	t (secs.)	Room Temp. (°C.)	Rdg. No.	% G	t (secs.)	Room Temp. (°C.)
1	8.3	43.2	23.3	7	58.5	133.0	
2	16.7	59.8		8	66.7	186.0	
3	25.0	34.8		9	75.0	256.8	
4	33.1	62.0		10	83.0	158.0	
5	41.5	98.2		11	91.5	186.0	23.4
6	50.0	122.2					

TABLE V
Series 4

Rdg. No.	% G	t (secs.)	Room Temp. (°C.)	Rdg. No.	% G	t (secs.)	Room Temp (°C.)
1	25.0 (Constant)	154.8	24.0	11		118.6	24.3
2		159.2	24.0	12		96.4	24.1
3		144.2	24.0	13		108.2	24.2
4		156.8	24.0	14		108.6	
5		154.0		15		100.6	24.2
6		115.8	24.1	16		106.4	
7		116.8		17		106.6	24.5
8		96.2	24.2	18		101.6	
9		114.4		19		109.8	24.6
10		98.4					

TABLE VI
Series 5

Rdg. No.	% G	t (secs.)	Room Temp. (°C.)	Rdg. No.	% G	t (secs.)	Room Temp. (°C.)
1	66.7 (Constant)	217.8	24.4	5		194.0	
2		243.4	24.6	6		220.2	24.9
3		224.2	24.7	7		213.4	24.9
4		189.2	24.9				

TABLE VII
Series 6

1	66.7 (Constant)	231.6	24.9	5		237.2	
2		231.0	24.8	6		200.4	24.6
3		246.6		7		205.4	
4		209.2	24.7	8		260.8	

TABLE VIII
Series 7

1	90.0 (Constant)	248.4	24.8	4		209.8	
2		241.4		5		240.0	
3		225.6		6		256.6	25.0

TABLE IX
Series 8

1	95.0 (Constant)	138.4	24.4	4		113.2	24.6
2		133.0		5		129.2	
3		136.2					

TABLE X

Series 9

Rdg. No.	% G	t (secs.)	t_{av} (secs.)	Room temp. (°C.)
1	16.1	99.8		
2	33.3	165.6		24.6
3	38.3	172.4		24.6
4	43.5	164.2		24.5
		162.2	163.2	
5	46.6	171.6		24.3
6	50.0	233.0		
7	55.5	241.2		
		265.8	253.5	
8	58.5	300.6	296.8	24.5
		293.0		
9	61.6	369.2		24.7
		373.8	371.5	24.2
10	63.3	188.4		
		272.0		24.4
		221.4		24.6
		224.0	226.4	24.6
11	66.7	273.6		24.7
12	70.0	282.7		24.7
		256.8		24.6
		291.6	277.0	
13	75.0	283.8		24.7
14	78.3	271.4		24.7
15	83.0	267.8		24.7
16	85.0	321.0		24.6
		285.0	303.0	
17	86.8	273.4		
18	88.5	267.7		24.6
19	90.0	261.4		
20	91.5	276.4		24.5
		243.6	260.0	
21	93.6	230.4		24.6
22	95.0	227.8		
23	96.5	218.0		
24	98.0	108.4		
25	99.2	156.0		
		123.6	139.8	24.4
26	99.6	150.0		

TABLE XI

Series 10

Rdg. No.	% G	t_A	$(t_A)_{av.}$	Temp.	t_B	$(t_B)_{av.}$	Temp.
1	3.3	41.6		22.0	33.2		
		36.6			35.2		
		31.2	36.5		47.6	38.7	
2	10.0	46.6		22.0	66.0		22.0
		81.2			73.2		
		59.4			75.4	71.5	
		78.4		22.0			
		72.2					
		83.4	70.2				
3	20.0	109.0		22.0	110.8		
		116.4			115.4		
		121.2	115.5		126.8	117.7	21.8
4	25.0	144.2		23.5	136.6		23.6
		150.0		23.6	141.8		23.6
		140.0	144.7	23.6	152.8	143.7	23.6
5	30.0	168.2		21.9	135.4		
		184.6		22.0	152.0		
		204.8	185.9	22.0	147.0	144.8	
6	40.0	225.4		22.0	222.4		
		216.4		22.1	221.8		22.1
		223.4	221.7	22.1	229.8	224.7	22.1
7	50.0	302.6		23.0	282.8		22.9
		285.6		22.8	284.6		23.0
		296.4	294.9	22.9	278.8	282.1	23.0
8	55.0	292.0		22.9	257.0		22.9
		293.8		22.9	277.4		22.8
		317.6	301.1	22.9	245.2		22.9
					283.3	265.8	22.9
9	60.0	342.6		22.8	268.0		23.0
		249.2		23.0	282.4		22.9
		309.8	333.9	22.9	273.8	274.7	22.8

TABLE XI (Continued)
(Series 10 Cont.)

Rdg. No.	% G	t_A	$(t_A)_{av.}$	Temp.	t_B	$(t_B)_{av.}$	Temp.
10	65.0	317.6		23.0	279.2		22.9
		311.6		23.0	289.4		22.9
		344.2	324.5	22.9	263.4	277.3	23.0
11	66.7	300.8		22.0	253.0		22.1
		286.6		22.0	270.2		22.1
		297.6	295.0	22.0	261.8	261.7	22.0
12	70.0	374.4		22.9	298.6		22.9
		360.2		22.9	285.0		22.8
		342.2	358.9	22.9	272.6	285.4	
13–1	75.0	304.4		24.0	315.8		24.0
		329.6		24.0	358.0		24.0
		334.8	322.9	24.0	273.8	315.9	24.0
13–2		280.2		21.8	260.6		
		298.0		21.9	246.4		
		296.4	291.5	22.0	290.6	265.9	22.0
14	80.0	274.6			316.6		
		279.6		22.1	284.0		
		251.4	280.6	22.0	314.6	305.1	
15	85.0	281.2		24.0	293.4		24.0
		246.8		24.0	307.0		24.0
		272.4	266.8	24.0	314.0	304.8	24.0
16	90.0	286.2		21.5	269.4		22.0
		234.8		22.0	300.0		22.0
		367.6	296.2	22.0	273.2	280.9	
17	95.0	324.4		22.0	186.2		
		336.0		22.0	244.0		22.0
		384.0	348.1	22.0	205.0	211.7	
18	98.0	220.8		22.0	219.4		
		325.2			214.8		
		277.4	274.5	21.9	234.4	222.9	22.0

TABLE XI A
Series 10, Summary

Rdg.	% G	t_A	% m.d.	% e.d.	t_B	% m.d.	% e.d.	$\frac{(t_B - t_A)}{(t_A)} \times 100$	Temp. Range
1	3.3	36.5	9.8	28.3	38.7	15.5	37.1	+ 6.0	22.0
2	10.0	70.2	16.3	47.0	71.5	5.1	13.1	+14.5	22.0
3	20.0	115.5	3.8	10.5	117.7	5.1	13.5	+ 1.9	21.8–22.0
4	25.0	144.7	2.4	6.9	143.7	4.2	11.2	− 0.7	23.5–23.6
5	30.0	185.9	6.8	19.5	144.8	4.3	11.5	−22.0	21.9–22.0
6	40.0	221.7	1.6	4.1	224.7	1.5	3.6	+ 1.0	22.0–22.1
7	50.0	294.9	2.1	5.8	282.1	0.8	2.1	− 4.3	22.8–23.0
8	55.0	301.1	3.6	8.4	265.8	5.1	14.3	−11.7	22.8–22.9
9	60.0	333.9	4.7	11.7	274.7	1.8	5.2	−17.6	22.8–23.0
10	65.0	324.5	4.0	10.0	277.3	3.3	9.4	−14.5	22.9–23.0
11	66.7	295.0	1.9	4.8	261.7	2.2	6.6	−11.3	22.0–22.1
12	70.0	358.9	3.1	9.0	285.4	3.0	9.1	−20.5	22.8–22.9
13	75.0	322.9 (A-1)	3.8	9.4	315.9 (B-1)	8.9	26.5	− 2.2	24.0
		291.5 (A-2)	2.6	6.1	265.9 (B-2)	6.2	16.5	− 8.8	21.8–22.0
14	80.0	280.6	6.4	9.6	305.1	4.6	11.5	+ 8.8	22.0–22.1
15	85.0	266.8	6.6	17.0	304.8	5.7	14.0	+ 8.8	24.0
16	90.0	296.2	16.1	44.7	280.9	4.5	10.9	− 4.4	21.5–22.0
17	95.0	348.1	10.7	30.0	211.7	8.8	22.6	−39.4	23.3–23.6
18	98.0	274.5	13.0	39.5	222.9	3.4	8.8	−18.7	21.9–22.0

TABLE XII

Data of a General Nature for Series 1 to 10 inclusive

Series	continuous time val (hrs.)	Total no. of individual rdgs.	Room temp. range (°C.)	G→C	C→G	Percentage range, of gasoline
1	Not recorded	10	22.0–22.2	X		1.7–98.0
2	$3\frac{1}{2}$	26	23.1–23.3	X(rdgs. 1 to 11)	X(rdgs. 12 to 26)	0.8–98.8
3	$1\frac{3}{4}$	11	23.3–23.4	[H_2O→ Na Cl sol. (rdgs. 1 to 3)]	[Na Cl sol H^2O (rdgs. 4 to 11)]	(Percentage H_2O) 8.3–91.5
4	$2\frac{1}{4}$	19	24.0–24.6	X		Constant at 25.0
5	1	7	24.4–24.9	X		Constant at 66.7
6	1	8	24.6–24.9		X	Constant at 66.7
7	$\frac{3}{4}$	6	24.8–25.0		X	Constant at 90.0
8	$\frac{1}{2}$	5	24.2–24.6		X	Constant at 95.0
9	$5\frac{1}{4}$	38	24.2–24.7	X (points 1 to 4)	X (points 5 to 26)	16.7–99.6
10	$58\frac{1}{2}$	118	21.9–24.0	X (whole range)	X (whole range)	3.3–98.0

Series 1

The liquid being added was poured by hand somewhat gently down the glass wall at one corner of the tank. Only one reading was taken at each abscissa value. The results are presented graphically in Fig. 4. The first four points, for volume percentages[1] under 20, agree with the results of both curves 2 and 10.

Series 2

Here also each of the plotted points, a total of 26, represents only a single run. For points 1 to 11 the gasoline (a word that will be abbreviated to the letter G) was added in the same manner as before, but more slowly. For adding the CS_2 (which will be abbreviated to the letter C) to the G, points 12 to 26, a glass tube about 4 mms. internal diam. was placed so that its lower end rested upon the bottom of the tank near one corner, and the liquid was poured down this tube, which prevented contact between the two liquids until the liquid being added, in this case the heavier one, was already at the bottom

[1] The percentages of liquid added were volume percentages throughout the present work.

of the tank. The tube was then removed to permit closing of the tank cover. Comparison of curves 1 and 2, Fig. 4, indicates that there was a pronounced "initial stir" incidental to the adding of one liquid to the other, before the start of agitation by the stirrer itself. In curve 2 the valley between 50 and 90% might be explained by supposing that the initial stir is greater in this region, meaning that the initial stir for C⟶G is much greater than for G⟶C, and greatest where the proportion of C lies between about 15 and 35% (85 and 65%, respectively, of G). The question arises as to why read-

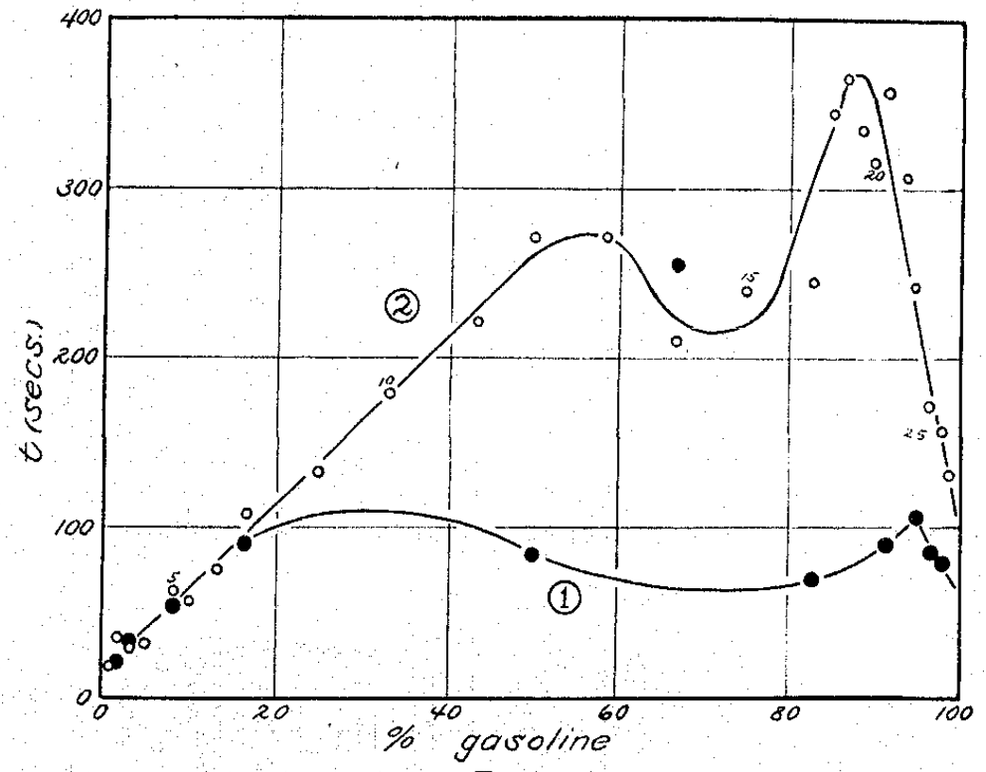


FIG. 4
Curves for Data of Series 1 and 2 for the mixing of Gasoline and Carbon Bisulphide

ings 12 and 13, representing larger percentages (50 and 58.5 respectively) of C, should agree with the preceding readings, G⟶C, of this series. This behavior is in harmony with the more reliable curve 10, Fig. 6. Over the percentage range mentioned (65 to 85% G) it is more definitely a case of C striae in G, while in the neighborhood of 50% G, there is more indefiniteness in this respect. The peak of the curve at point 18, and the quite consistent drop from there on, indicates that the effect of the initial stir has become much less, if not negligible, for percentages of C below about 15.

It seems obvious that the failure of curve 1 to rise much above 100 secs., and the broad valley, are explainable by a correspondingly greater amount of initial stir.

The apparently linear relation up to 50% in curve 2 will be discussed in connection with curve 10.

Series 3

The two liquids here are distilled water and a concentrated solution of common salt in distilled water. For readings 1 to 3 the water was added to

the salt solution by permitting it to flow gently, poured by hand, down the glass wall at one corner, but for readings 4 to 11, the glass tube was used in the same manner as with series 2. The curve, Fig. 5, rises quite uniformly to about 75%, where there appears to be a maximum. This indicates that "striae of salt solution in water" are longer-lived than "striae of water in salt solution," if the line of distinction between the two kinds is regarded as being at the abscissa value of 50%.

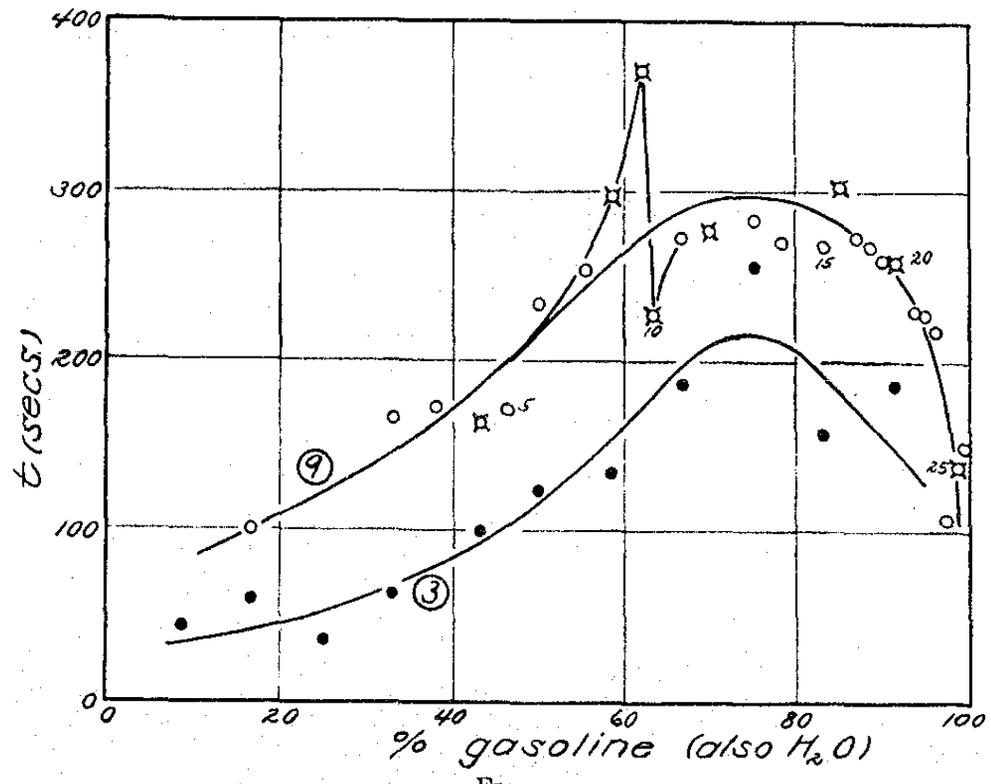


FIG. 5
Curves for Data of Series 3 and 9, respectively, for Saturated Solution of Sodium Chloride in Water and Water, and for Gasoline and Carbon Bisulphide

Series 9

Here the glass tube was used in a uniform manner throughout the whole series. Points 1 to 4, G⟶C; points 5 to 26, C⟶G. The liquid being added, was poured directly down the tube, the lower end of which rested on the bottom of the tank. Nine of the plotted points, starred in Fig. 5, represent average values of two or more separate readings each, as given in Table XIII. A fairly consistent rise in the curve to a point a little above 60%, and also some filling up of the valley that was observed in curve 2, Fig. 4, are seen. Since points 8 and 9 represent the means of two values each, with only a slight difference in the individual readings entering into each mean, they are regarded as acceptable. Point 10 is the mean of four readings, but the mean deviation is high, 10.0%. The four readings averaged for point 10 were taken inside a period of about 1½ hours., while the room temperature did not vary more than 0.3° C. Some meaning might possibly be attached to the increase in the slope from points 1 to 9, and the abrupt drop from point 9 to point 10, between 60 and 65%. Points on both sides of this drop were obtained with

the same condition, C⟶G. Such a drop fails to appear in curve 10, Fig. 6, based on more thorough measurements, unless the sag in curve 10B, C⟶G, has the same interpretation as the abrupt drop in curve 9. Neglecting point 9 with its high value of the time of mixing, curve 9 appears to have a maximum in the neighborhood of 75%, about the same place as that for curve 3, with its different materials and more meager data.

TABLE XIII

Cases in Series 9 where more than One Reading was taken at a Given Percentage.*

Point number	Number of separate rdgs.	% mean dev.	Point number	Number of separate rdgs.	% mean dev.
4	2	0.6	12	3	4.9
7	2	4.9	16	2	5.9
8	2	1.3	20	2	6.3
9	2	0.6	25	2	11.5
10	4	10.0			

* These points are starred on the curve.

Although the linear relation up to 50%, common to curves 2 and 10, is not found here, perhaps because of initial stir, only one reading was taken below 20%, and this agrees with those curves. The tube was used in series 9 for adding the second liquid, which was poured into the tube by hand, and the rate of flow may have been greater than in series 2, where the liquid was poured without the use of a tube. At any rate, the manner of adding was different when the second liquid flowed through the tube, entering the first liquid near the floor of the tank, from what it was when it entered by flowing down the tank wall.

Series 10

The manner of adding the second liquid was now modified. A glass funnel was narrowed at its nozzle end so that the liquid flowed much slower than before, down a glass tube about 9 mms. internal diam., causing less initial turbulence in the tank. This method was used uniformly throughout the series, with point 17B the sole exception, where the C (5% of total volume) flowed slowly down an inside angle of the walls of the tank, as in series 2, first part. Separate measurements were made of the time for constant volumes to flow into the tube from the funnel, filled initially to the brim, for each test, and holding 22 cc. Successive measurements resulted: for C,— 16.2, 18.8, 18.6, 18.4, average 18.0 secs; for G, — 26.2, 26.2, 31.2, 33.6, 30.6, average 29.6 secs. The longer time of flow for the gasoline may help to account, by a greater initial stir, for the slight remaining valley in curve 10B. An adjustable control would insure a uniform volume rate of flow into the tank for both liquids.

The same samples of gasoline and CS_2 were used throughout series 10.

Fig. 6 shows the two curves of series 10 superposed: (A), G⟶C over the whole range of percentages of gasoline, $3\frac{1}{3}$ to 95; and (B), C⟶G, over the

same range. Each curve has a total of eighteen points at the same percentage values. Each point represents the mean of three individual readings, with two exceptions (Table XI, 2A and 8B). During the four consecutive days in which the data of series 10 were being taken (see above), both the A and the B readings, for the different numbered points on the curves, were obtained as follows: 1st day, 13–1, 15; 2nd, 4, 7, 9, 10; 3rd, 8, 11, 12, 13–2, 14; 4th day, 1, 2, 3, 5, 6, 16, 17, 18.

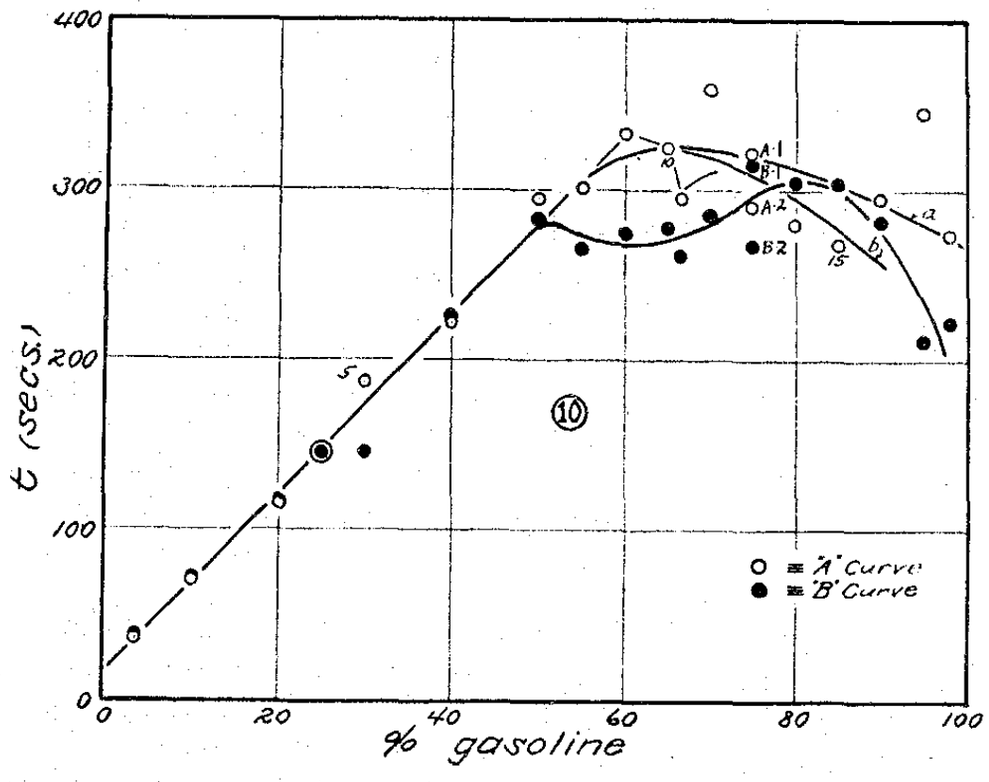


FIG. 6
Curves for Data of Series 10, for Gasoline and Carbon Bisulphide

The valley that was so pronounced in curve 2 has disappeared from curve 10A, although an abrupt drop occurs just above 60%, similar to that of curve 9; at any rate an erratic tendency is evident above that point. Apparently the initial stir has been reduced below an amount sufficient to cause a definite valley between 60 and 85% as in curve 2. Further, in view of the fact that for series 2 the flow of liquid into the tank was not nearly so well controlled as to manner and rate, as for series 10, the initial stir seems to have been practically eliminated up to 60% for curve 10A, and up to 50% for curve 10B, as indicated by the similar slope values of curves 2 and 10 between 0 and 50%.

The valley has not disappeared entirely from curve 10B. It is not surprising that this curve does not agree throughout with 10A. The conditions of adding the second liquid, while being the same as far as the mechanical arrangement of funnel and tube were concerned, were actually different. Not only was the rate of flow different, as described above, but, for C⟶G, the lower end of the glass tube (see discussion, series 2) rested on the tank floor near one corner, and the C being introduced spread out on the bottom

of the tank because of its greater density, lifting the G bodily. For G⟶C, the G being introduced rose in the vicinity of the tube immediately to the surface, and spread out on top where it floated (the two densities are of the respective orders 0.70 and 1.25), leaving a fairly well defined interface between the two liquids. Under these circumstances one might perhaps expect the valley to appear in the A curve, G⟶C, rather than in the B curve where it was found. But the evidence from the valley effect is that the initial stir 50% G, is greater for C⟶G.

For point 2A, the time t_A, for the first three readings taken, gave the high mean deviation value of 20.0%. Three additional readings were then taken, whose m.d. came out 5.0%. The low values of the first and the third of the six individual readings are unexplained, unless on the basis of the unequal percentages of the two liquids. The first three gave a mean of 62.4, the second three a mean of 78.0 secs. The mean of all six runs was 70.2 secs., and the m.d., 16.3%, values that were retained. Point 8B represents the mean of four readings, instead of three. For point 13B the m.d. was rather high, 8.9 %. The six readings for this point were repeated, and the m.d. values for both 13A and 13B were thereby lowered. The first values of t_A and t_B were higher than the second values, by 10.7 and 18.7% respectively, and the lower of the first two values, 315.9, was 8.3% higher than the higher of the second values, 291.5 secs. In each case the A value was higher than the B. The different values of the two A points may be merely a manifestation of the somewhat erratic behavior between 60 and 80%, already mentioned. Whether the slightly higher temperature of the room tended to increase the time values is not known. Points 17A and 18A both are located well above the corresponding points on the B curve. For point 17, all three individual readings of the A group are well above the B group, the lowest reading of the A group being 324.4, and the highest of the B group 244.0 secs. One might expect these two A points to be below the B points, as is the case with points 14 and 15, since adding 95% G to 5% C as for point 17, might be expected to cause greater initial stir than adding 95% C to 5% G. But the strong tendency of the G to float on the C is to be kept in mind.

That the locations of both the A and the B points from 8 to 15 inclusive (55 to 85%) justify reliance, is indicated by the fact that for points 8 to 12 inclusive (55 to 70%) every one of the three individual A readings lies above all three individual B readings of the mixing time in every case, while for points 14 and 15 the reverse is true, and only for point 13 is there overlapping of the individual readings of the two sets. For points 6 to 12 inclusive (40 to 70%), curve A, all the mean deviations, Fig. 7, are below 5%, averaging 3%, while for curve B the highest is that for point 8, 5.1%, and the average is only 2.5%, so that the separation of the two curves at about 50%, leaving a sag in curve B, is regarded as a real effect. For the present, the sag, or remaining valley, in curve B may be interpretated as the effect of some remaining initial stir over the percentage range of, say, 60 to 80.

Curve 10B from 55% up is fairly consistent with curve 9 over this range.

The two curves, A and B, can be regarded as coinciding up to 50%, and the relation here is apparently linear. The slope, 5.2, agrees quite well with that of curve 2, which is 5.0 in this region. In curve 2 the apparently linear relation up to 50% rather indicates in itself either absence, or small amount, of initial stir, for it is hardly presumable that over as much as half the range of abscissa values, an appreciable time of initial stir subtracted in each case from the correct total time of stir, would leave a linear relation, although conceivably it might. At any rate, the slightly steeper slope of curve 10 may be interpreted as a further reduction of initial stir over this percentage range, or even its approximately complete removal, in view of the small change in the slope with the much improved conditions of adding the second liquid.

It is perhaps surprising that the two curves agree at all up to 50%. Better agreement might be expected over a central range, say 30 to 70%, where for both curves A and B the volume of liquid added was more nearly comparable to that already in the tank. The agreement observed may be accepted as being in itself evidence that the initial stir over this range was now negligible. Otherwise it would be necessary to interpret these similar time readings taken under dissimilar conditions as meaning that the initial stir time for percentages of G up to 50, is dependent only upon the % G, not upon whether the smaller or the larger proportion of liquid was being added, and further, that the actual stir time less the initial stir time leaves, over the range 0 to 50%, a linear relation.

To regard the initial stir as having been equally well eliminated from curve 10A between 60 and 80% is not entirely justified, for we do not know how much higher the peak might go with further conceivable reduction of initial stir over this range. But unless there is a pronounced increase in the slope of curve A above 60%, which is not suggested by the linear relation up to that point, the actual peak seems to have been approximately attained.

Corresponding points on the two curves below 20% show good agreement, and those above 80% fair agreement, with the exception of point 17. This might be taken to indicate the removal of the initial stir, not only in these regions but over the entire range. For if adding say 6 cc. (10%) G to 54 cc. C gave the same mixing time as when 54 cc. C was added to 6 cc. G, there could hardly have been an appreciable amount of initial stir in either case. It is difficult to imagine an appreciable initial stir that is the same in each of two cases representing such dissimilar conditions in the bringing of the two liquids together. But this view would require some other explanation for the remaining sag in curve B, than that alone of remaining initial stir.

Beginning at 65% two branches are drawn for curve A. The upper one, a, gives about equal weight to all the A points in this region, while the lower branch, b, neglects the last three points at 90, 95, 98% respectively. But in either case a maximum is indicated in curve A at about 65%. If the sag in curve B is rightly explained by initial stir that has not yet been removed, then curve B may be assumed to have a maximum at about the same place. The more general assertion seems warranted, that a maximum exists between 60 and 80%. This is borne out by curve 9. The reason for the somewhat higher

points on curve 2 in the neighborhood of 90% is not known, but it can be explained by the greater tenacity of the striae of C in G, which is indicated particularly by the existence of a maximum at a point above 50%.

If below 50% we should speak of "striae of C in G", a maximum at a point above 50% would mean, in general, that striae of C in G are longer lived, or "tougher," than striae of G in C. This is shown consistently in curves 2, 9, and 10. Some readings taken subsequently with 90% of another sample of G, showed a definite tendency of the fine striae of C in G to linger before final disappearance. These additional readings, taken with 59 cc. G to 1 cc. C were: A,— 220.8, 325.2, 277.4 secs., average 274.5 secs., m.d. 13.0%; B,— 219.4, 214.8, 234.4, average 222.9 secs., m.d. 3.4%; room temperature 22.0°C.

The somewhat abrupt separation of the two curves at 50% should be further noted. An abrupt separation in itself would call for interpretation, while the fact that such appears to occur at 50% may be of additional interest. Possibly the rather arbitrary view that percentages of G less than 50 give "striae of G in C," while percentages of G over 50 give "striae of C in G," finds here some experimental justification. Perhaps the particular location of the maximum itself is the demarcation between the two types of striae. Or is there a transitional region, say from 50 to 80%, where the situation is ambiguous?

For the condition C⟶G, the C entering at the bottom of the tank, at any rate after the minimum necessary amount of C has left the end of the tube and spread out to form a continuous layer over the whole of the tank floor, flows into C, not into G, and any initial stir must be an effect at the interface. Due to the currents set up by the entrance of the second liquid there must be considerable movement between the two liquids at the interface, even for C⟶G. For G⟶C the conditions of entrance of the liquid being added are different from the other case. But curves 10 indicate absence of appreciable initial stir up to at least 50% abscissa value, so that over this range relative motion between larger masses of the two liquids must produce negligible initial stir. The natural explanation is a strong tendency of the two liquids to maintain the interface. Further, the apparent elimination of initial stir up to 50% indicates that mere contact between the liquids results in no marked initial mixing, even when one of the liquids (that being added) is moving relative to the other, which in turn is evidence of a definite interface maintained by strong surface tension forces, so that the two liquids are, in a sense, mutually exclusive. If such behavior is shown by thicker layers of the two dissimilar liquids in contact, it will be expected to continue even after the striae have become quite thin.

The mixing process in general must consist in the production of striae, by mechanical agitation of the kind described, that are made finer and finer by the agitation until they finally "disappear." This disappearance may be nothing more than the breaking up of the fine striae, regarded as true films, into microscopic or ultra-microscopic droplets, in the same way a soap bubble bursts into fine droplets of soapy water. It is known that CS_2 and gasoline tend to "stratify," or separate out, if the mixture is permitted to stand after

the liquids have been thoroughly stirred together until the striae have disappeared. This behavior may consist of a gradual gathering of the minute droplets of a given kind of liquid into layers because of the different densities of the two liquids.

Curves 1, 2, 10, all show consistently a y-intercept of about 15 secs., if the experimental curve is extrapolated to the y-axis. The slope may have much higher values between zero and the lowest percentage, 3⅓, subjected to test. This positive y-intercept is evidence against appreciable initial stir, unless the latter is masked by an unknown agent having an opposite effect. Systematic error could account for such an intercept. It would include the error in assuming that the speed of the motor is reached instantly on closing the switch, but this error could not have exceeded 2 secs.

The question arises whether two stages of the mixing are to be recognized: (1) the mechanical dividing up of the two constituent liquids into striae sufficiently small so that as very thin films they will start to break up into minute droplets as suggested: and (2) the breaking up of the striae in this manner. It may be supposed that the breaking up in itself requires time, after the striae have been reduced sufficiently in size,—with some action of a physico-chemical nature. These two supposed stages of the mixing process may conveniently be termed the "primary mixing" and the "secondary mixing" respectively. The total mixing time as measured in the present experiments would then include the "primary mixing time" and the "secondary mixing time," with the primary and the secondary mixings proceeding simultaneously, at any rate overlapping.

On such a basis the consistent positive y-intercept shown by the experiments may be explained as follows. (It must be noted that this "consistent positive y-intercept" is that of an extrapolated experimental graph whose lowest abscissa value was 3⅓%.) The linear experimental curve up to an abscissa value of 50% is the resultant of two curves, one for the primary, the other for the secondary mixing time. Writing the experimental formula $y = mx + b = y_1 + y_2$, where y is total mixing time, m is slope, x is volume percentage of gasoline, b is the positive y-intercept, y_1 the primary mixing time, and y_2 the secondary mixing time, it is seen that y_1 is either a function of x, or a constant. The latter event does not seem likely, so that both y_1 and y_2 are functions of x. Both must then be linear functions of x, so that $y_1 = m_1x + b_1$, $y_2 = m_2x + b_2$, and $y = (m_1 + m_2)x + (b_1 + b_2)$. Assuming that $b_2 = 0$, then $b_2 = b$, and $y = (m_1 + m_2)x + b$. While the sum $(m_1 + m_2)$ is known, neither m_1 nor m_2 is known. The physical meaning is that if the two liquids could in some imaginary way be brought together with the striae already fine enough for the "disappearance" process, or secondary mixing, to begin, the experimental graph would be a straight line through the origin. It is possible to regard the observed intercept as belonging exclusively to the secondary mixing time, or as being shared by both the primary and the secondary mixing time, so that neither b_1 nor b_2 is zero.

Curve 10B drops toward the 100% position on the abscissa axis in a manner similar to that of curves 2 and 9. It is to be recalled that for both of these

curves in the range of larger percentages, the condition of adding was G⟶C, the same as for curve 10B. The higher time values for curve 10A at 90% and above, indicate that there is more initial stir in this region, for curve B than for curve A. The high values of both A and B here, where it is a clear case of "striae of C in G," compared with the low time values from 0 to 10%, where it is a clear case of "striae of G in C," affords a comparison of the two types as to their staying powers, or toughness.

In curve 2, where readings were taken at a larger number of points than for 10B, the roughly linear relation shown by the six plotted points above 90%, suggests a positive y-intercept on the line x = 100%. This can be interpreted as meaning that a distinction is to be drawn between "primary mixing" and "secondary mixing" for "striae of G in C," while this distinction has already been drawn for "striae of C in G."

A comparison of curves 10 and 2 is a little objectionable because each point on the latter is based on a single reading only, while on the former each point is based (with one exception, point 13) on three individual readings. And yet the linear relation appearing in curve 2 indicates a degree of consistency not to be looked for in very erratic results, and consistency is further indicated by the similar behavior of the more thorough curve 10.

Reproducibility

The five successive series, 4 to 8 inclusive, serving for reproducibility tests, were all made with gasoline and carbon bisulphide.

Series 4. For readings 1 to 11 inclusive the G was added to the C by pouring down the corner of the tank walls, tilting the tank somewhat for the purpose. There was no observed reason for the abrupt drop of about 30% in the mixing time after the 5th reading. A rise in the commercial voltage on the motor generator supply may have occurred, but no voltage test was made at that time. Starting with the 12th reading, the G was poured down the glass tube, its lower end resting on the tank floor near a corner. This modification had no very appreciable effect on the readings, except perhaps to make them less erratic. For readings 12 to 19 inclusive the mean time value was 104.8 secs., and the m.d. 3.7%.

Series 5. The G was added by means of the glass tube, in the same manner as for the latter part of series 4. Probably the volume, 66⅔%, of the liquid being added, G, which was greater than the volume of C already in the tank, accounts for the larger percentage deviations than in the preceding series. But this percentage value falls within the region where somewhat erratic results appeared in curve 10A. The mean value of all seven readings was 214.6 sec., m.d. 6.3%.

Series 6. This series was started within 15 mins. of the finish of series 5, and the second liquid, in this case C, was added in the same manner as in series 5. Some variation in the voltage on the motor was observed, but its effect on the results was probably unimportant. The mean value of all eight time readings was 227.8 secs., m.d. 7.5%.

Series 7 and 8. The manner of adding was the same as that for series 5 and 6. In series 7 and 8 the average time values were 237.0 and 130.0 secs. respectively, and the m.d. value was 5.4% in each case.

Series 10. Preceding the taking of data for series 10, voltage control, consisting of voltmeter and rheostat, was installed locally at the apparatus. This more extensive series, giving curves A and B, comprised more than a hundred individual readings, or runs, and was in itself a reproducibility test. The mean deviation and the extreme deviation values (Table XIA), shown by the graphs of Figs. 7 and 8 respectively, indicate the degree of reproducibility, where each average time value represents three individual readings, with 2A and 8B as the only exceptions, as mentioned already. Curve A, G⟶C, is displaced (see Fig. 7, representing the mean deviations) somewhat to the left of curve B, C⟶G, for the higher abscissa values. In curve A, over the range 20 to 80%, the m.d.'s, with one exception, fall below 5%, and for curve B these values average almost as low. Table XIV presents the average % m.d. and the average % e.d. for readings 4 to 13 inclusive, and for readings 1 to 18 inclusive, for both the A and the B curve, in a form suitable for comparison. In this table the two mean values for reading 13 were used for both the A and the B cases, so that for readings 4 to 13 a total of 11 readings, and for readings 1 to 18 a total of 19 individual readings, were averaged. Readings 4 to 13 cover the percentage range 25 to 75 inclusive, where the m.d. values fell usually below 5%, and the e.d. values below 20%.

TABLE XIV

Average Percentage Deviation Values, Series 10, for Two Sets of Readings, 4 to 13 inclusive, and 1 to 18 inclusive

Curve	Mean Deviation		Extreme Deviation	
	Readings 4 to 13	Readings 1 to 18	Readings 4 to 13	Readings 1 to 18
A	3.33	6.28	8.70	16.96
B	3.76	4.95	10.55	13.03

Comparisons among the eight average values in Table XIV, of the mean and the extreme deviations, will be made in three specific ways: (1) for the same curve (either A or B), a comparison of the two sets of readings (4 to 13, and 1 to 18) first on the basis of m.d., and then on the basis of e.d.,; (2) for one of the two sets of readings, a comparison of the two curves on the basis first of m.d. and then of e.d.,; (3) for the same curve, a comparison of the two deviations on the basis of the same set of readings. Without interpretations being made here of the rough agreements observed, it is interesting to make the comparisons.

(1)For both curves A and B, both the average % m.d. and the average % e.d. are higher for readings 1 to 18 than for readings 4 to 13 by the respective amounts 88 and 95% for curve A, and 32 and 23% for curve B. The magnitudes of the members of either pair of these four percentages are roughly comparable.

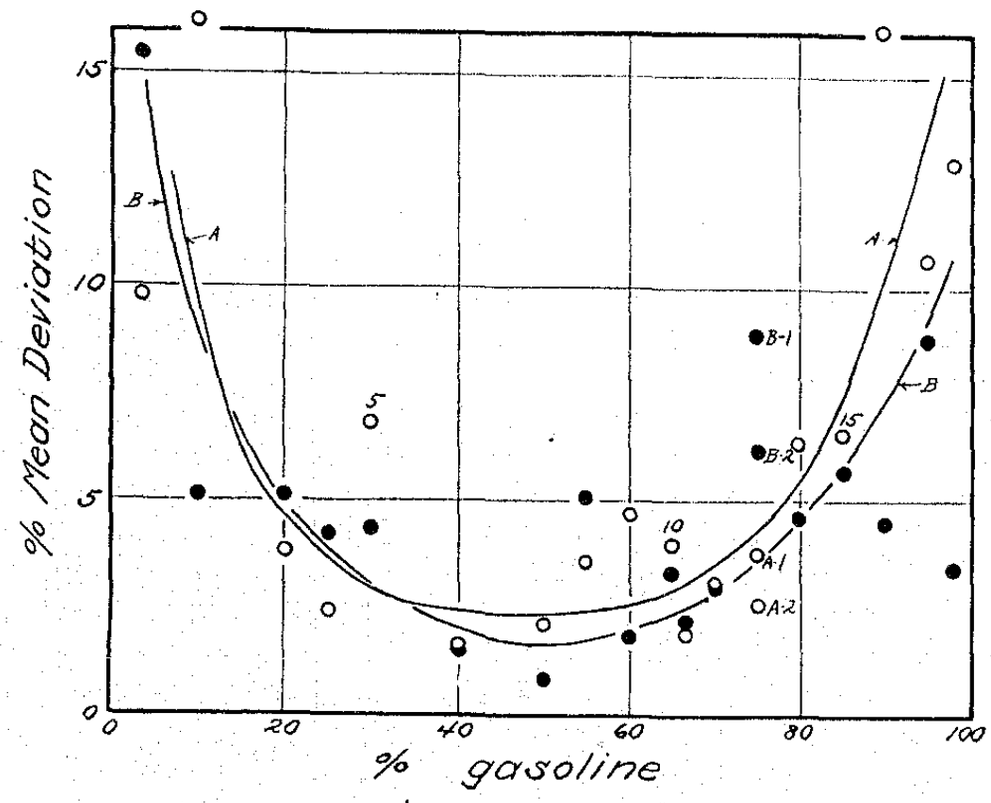


FIG. 7
Reproducibility Tests: Mean Deviations, Series 10

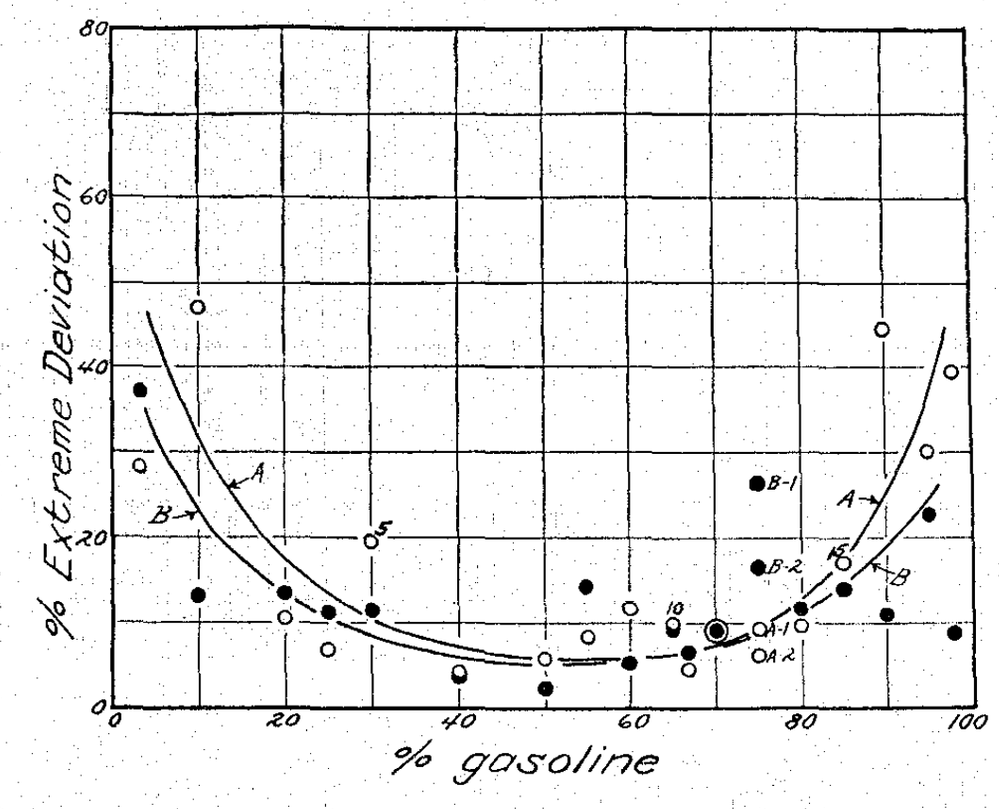


FIG. 8
Reproducibility Tests: Extreme Deviations, Series 10

(2) For readings 4 to 13, both the m.d. and the e.d. percentages are higher for curve B than for curve A by the respective amounts 13 and 21%, while for readings 1 to 18 both the m.d. and the e.d. are lower in curve B than in curve A by the respective amounts 21 and 23%. All these four percentages have roughly comparable magnitudes.

(3) For both curves A and B, the e.d. is higher than the m.d. for both sets of readings by the respective amounts, 195 and 185% for curve A, and 170 and 163% for curve B. Again, all four of these percentages are roughly comparable.

Summary and Conclusions

1. A method of measuring the "time of mixing" of two or more transparent liquids, not too readily miscible, making use of the aberrational effect of the striae upon a beam of transmitted light, was tested experimentally and found available for such work. The present work was the experimental testing of a method rather than the gathering of an extensive mass of experimental data for interpretation on the basis of physical chemistry.

2. It was found that the "disappearance" of the striae under the present experimental conditions occurred quite abruptly, and that this made possible a definition, and a fairly precise determination, of the time at which the mixing ends. This could be determined probably to within 3% of the total mixing time.

3. Using gasoline and CS_2, both commercial, as the two liquids, total volume constant at 60 cc., data were obtained at room temperature (22° to 24° C.) over an extreme volume percentage range of gasoline from 0.8 to 98.8% inclusive. The measured mixing times, under the given constant conditions of stir, varied with the percentage, from 18 secs. to 6.5 mins.

4. Incidental readings with water and a concentrated water solution of common salt as the two liquids, were taken at room temperature. Under the same mechanical conditions of stir as with the gasoline and CS_2, a series of 11 different readings, each at a different percentage, was obtained, over a volume percentage range (of water) from 8.3 to 91.5 inclusive, total volume constant at 60 cc., as elsewhere in the present work. This briefer test series gave a fairly consistent curve that was in general analogous to those with gasoline and CS_2. A maximum of from 200 to 250 secs. was indicated at a water percentage of about 75. This curve indicates that further useful results can be obtained with the method, with other materials than gasoline and CS_2, which are two liquids capable of forming well-defined and quite tenacious striae.

5. A progressively more complete elimination of "initial stir," or the stir incident to bringing the two liquids together in the present method, previous to starting agitation by the stirrer, resulted from successive improvements in mechanical conditions of the experiment, until in the most thorough series, no. 10, practically complete removal of the initial stir appeared to have been attained over the whole percentage range used, in the case of gasoline added

to CS_2, and in the reverse case practically complete removal over the range 0 to 50%, and almost complete removal over the remaining range.

6. Conclusions are drawn chiefly from series 10, which was obtained in more thorough manner, and is used as the basis of discussion and comparison. This series consisted of a total of 118 individual measurements of the mixing time at 18 different percentages of gasoline, from 3⅓ to 98.8 inclusive, and with at least three individual readings taken at each percentage, to be averaged, and also to serve as an incidental reproducibility test. Series 10 consisted of two series superposed, one for gasoline added to CS_2 (10A), the other for CS_2 added to gasoline (10B), each of the two series being taken with equal attention to thoroughness. Curves 10A and 10B were drawn from the data of the respective series, with the mixing time in secs. as ordinates, and the percentages of gasoline as abscissae.

7. Up to 50% abscissa value both the A and the B curves of series 10 coincide, showing (1) a linear relation with a slope of approximately 5.0, (2) for the extrapolated curve (extrapolated from 3⅓ to 0%) a positive y-intercept of 15 secs., and also (3) some evidence of a corresponding positive intercept on the vertial line x = 100%. A maximum time of mixing, of from 300 to 350 secs., was indicated from the results, for both cases A and B, located at about 65%. A maximum at this point appears to mean that "striae of CS_2 in gasoline" are longer lived, i.e. more tenacious, than "striae of gasoline in CS_2."

8. Not more than 15% at most of the positive y-intercept of about 15 secs. could be accounted for on grounds of known error. The presence of the intercept suggests that the process of mixing combines two types, or stages, a "primary mixing" during which the striae are being subdivided with little or no "disappearance," and a "secondary mixing" which includes the disappearance process, the two stages probably overlapping considerably, that is, existing together in the liquid medium being stirred. It was concluded that if two such stages of the mixing exist, then the mixing time for each is a linear function of the proportion percentage.

9. The question, what percentage of gasoline is to be regarded as dividing "striae of gasoline in CS_2," from "striae of CS_2 in gasoline," and the possibility of an intermediate type of striae (see next paragraph), were discussed. If at lower percentages, say 5 and 10, the term "striae of gasoline in CS_2" is used, which is quite justified it would seem, then the continuation of the linear relation above 50%, which means a continuation of essentially the same physical (mechanical) conditions in the liquid, requires that the demarcation between the two types of striae be located not at 50%, but at about 60% gasoline.

10. The entrance of somewhat erratic behavior at about 60%, especially where gasoline was added to CS_2, indicates that a transition occurs at this point to a somewhat different set of physical conditions in the liquid, and therefore some kind of modification in the nature of the striae. (The term "striae" in this article is defined as comprising that structure in the body of the liquid which produces aberration of light rays under experimental conditions such as the-

present.) At about 60%, then, the striae become either "striae of CS_2 in gasoline," as at, say, 90% gasoline, or striae of a transitional, perhaps ambiguous, type belonging to a range of gasoline percentages that begins at about 60 and extends to where the striae can be properly regarded as "striae of CS_2 in gasoline." The characteristics of the striae, particularly in the percentage range 60 to 80, merit further study.

11. The results showed a fairly high degree of reproducibility. This was indicated quantitatively by percent mean deviation and percent extreme deviation in successive determinations of the time of mixing at each of different percentages,—particularly in the case of the most thorough of the data, series 10,—covering the extreme percentage range over which measurements were made, and having at least three individual readings at each of the 18 percentages used, for both the case where gasoline was added to CS_2 (series 10A) and that where CS_2 was added to gasoline (series 10B). Curves for both these deviations show mean deviations as low as 0.8 and as high as 16.3%, and extreme deviations as low as 2.1 and as high as 47.0%, the higher values occurring, as would be expected, at either the very low or the very high gasoline percentages. The average mean deviation for percentages from 25 to 75 inclusive was 3.3 for series 10A, and 3.8 % for series 10B, and the corresponding extreme deviation values were 8.7 and 10.5%. For all 18 readings the average mean deviation values were 6.3 and 5.0% respectively, and the average extreme deviation values were 17.0 and 13.0% respectively.

12. A possible explanation of the disappearance of the striae is that they behave like liquid films in air, bursting to form minute droplets of the material.

In concluding this article the writer wishes to acknowledge some photographic assistance in the preliminary work from Mr. J. Elder, and assistance in mechanical construction at various times from Mr. L. P. Delsasso.

Department of Physics,
University of California at Los Angeles.

THE VELOCITY OF INTERACTION OF IONS

BY FREDERICK GEORGE SOPER

The examination of the rate of interaction of ions has shown[1] that the speed is considerably affected by the ionic strength of the medium; and increase in the ionic strength, which decreases the activities of the ions, actually increases, in certain cases, the speed of interaction. This behavior is in direct opposition to the simple activity theory of reaction velocity, and Brönsted has in consequence developed the theory that the important factor governing the rate of any chemical reaction is the ratio of the activity of the molecules or ions in their initial state to that in the critical state. His critical state is an unstable, highly reactive complex of the reagents and its rate of formation governs the rate of interaction. The expression derived for the speed, v, is

$$v = k\, C_A\, C_B \cdot \frac{f_A\, f_B}{f_X}$$

where C_A, C_B and f_A, f_B are the concentrations and the activity coefficients of the reactants respectively, and f_X the activity coefficient of the complex X. Comparison of the equation with the classical expression, $v = k_2\, C_A\, C_B$, shows that k_2 should vary proportionally to the factor $f_A\, f_B/f_X$. This factor is evaluated from the expression, $-\log f = 0.50\, z^2\sqrt{\mu}$, based on the Debye-Hückel theory, z being the valence of the ion and μ the ionic strength, leading to the equation[2]

$$\log k_2 = \log k + 1.00\, z_A z_B \sqrt{\mu} \qquad (2)$$

which connects the classical bimolecular velocity coefficient, k, with the magnitude and sign of the factor $1.00\, z_A z_B \sqrt{\mu}$.

The equation (2) is in good qualitative agreement with existing data on ionic reactions, the classical biomolecular constant being decreased on increase of ionic strength if the ions are unlike, whilst it is increased if the ions are of like sign. Whether it is correct, however, to regard the Brönsted equation (1) as a fundamental equation capable of application to all types of reaction including those in which neutral molecules interact, is doubtful, for an equation similar to the Brönsted equation (2) can be developed for *electrically charged* molecules by regarding the potential energy of the reacting ions as contributing to the critical increment of the reaction. [The equation differs from (2) only in the numerical factor multiplying $z_A z_B \sqrt{\mu}$ and appears to be in better agreement with the experimental data at present available.]

The idea of a critical reactive state arises from the dependence of reaction speed on temperature as expressed in the Arrhenius equation $d \ln k/dt = E/RT^2$, which necessitates some conception of activited molecules, the proportion of which in a given mixture is some exponential function of the tem-

[1] Brönsted: Z. physik. Chem., **102**, 169 (1922).

[2] Brönsted and Livingston: J. Am. Chem. Soc., **49**, 435 (1927).

perature. The form of activation is a matter of conjecture but since all forms of energy are subject to the same type of distribution law, observations are equally well explained whether one assumes the energy of activation to be kinetic, or rotational or to be due to molecular vibrations. Regarding the activation as kinetic, the number of molecules N_1 possessing kinetic energy greater than some value E is given approximately by $Ne^{-E/kT}$. Application of this distribution to a gaseous system containing N_A and N_B molecules of A and B respectively gives the proportion of the A and B molecules having combined energy exceeding E as $e^{-E/kT}$. The number of collisions per second between A and B molecules possessing combined energy E is thus proportional to $N_A N_B e^{-E/kT}$ and the speed, expressed in mols transformed per unit volume per unit time is given by,

$$v = k C_A C_B e^{-E/kT}$$

The application of this formula to reactions of neutral molecules in solution is apparently sucessful so long as one examines reactions in dilute solution. Its application to reactions between ions would be expected, however, to be modified by the possession of potential energy by the two reagent ions in virtue of their electrical charges.

If the ions are of like sign they will experience a repulsion as they approach each other and their combined kinetic energy must be correspondingly greater for effective collision than if the molecules were uncharged. This repulsion will depend upon the potential of the ions which on the Debye-Hückel theory is decreased with increase of ionic strength. Hence we should expect the number of molecules capable of reacting to increase with increase of ionic strength, since the repulsion decreases. Conversely, if the two reagent ions are of unlike sign, they will experience an attraction and their combined kinetic energy of approach will be augmented, causing a greater proportion of the molecules to be capable of reacting than if the molecules were uncharged. Increase of ionic strength by decreasing the potentials of these ions lessens the attraction and decreases the speed.

The potential energy possessed by the two reacting ions may be evaluated as follows. The total free electrical energy of a solution of n ions, found by charging them reversibly[1] is $\frac{1}{2}nze\psi$, where ψ is the potential at one of these ions due to the surrounding "ion atmosphere." Part of this electrical free energy resides in the medium, but change in the partial free electrical energy of the ions is attended simultaneously by a change in the electrical free energy of the medium. The total potential energy possessed by an ion in virtue of its charge is thus $\frac{1}{2}ze\psi$ and the potential energy possessed by a pair of ions with respect to their combination will be the difference of the total work done in charging the ions A and B and that done in charging a complex formed by collision of A and B. If the ions have charges z_A and z_B, the complex will have charge $z_A + z_B$ and the potential energy of A and B will be given by

$$\tfrac{1}{2} e\{z_A\psi_A + z_A\psi_B - (z_A + z_B)\psi_{A,B}\}$$

[1] Debye: Physik. Z., **25**, 97 (1924).

The potential ψ_i, at an ion i due to its surrounding ion atmosphere is given by

$$\psi_i = \frac{-z_i e\kappa}{D} = \frac{-z_i e}{D}\sqrt{\frac{4\pi e^2 \Sigma n_1 z_1^2}{DkT}} = \frac{-z_i e}{D}\sqrt{\frac{8\pi e^2 N\mu}{10^3 DkT}}$$

where n_i is the number of ions of the i'th kind per c.c. in the solution, e the charge on a univalent ion, N the Avogadro number, and k the gas constant per molecule.

Hence the potential energy of the pair of ions A and B

$$= \tfrac{1}{3}\left\{-z_A^2 - z_B^2 + (z_A + z_B)^2\right\}\left\{\frac{e^2}{D}\sqrt{\frac{8\pi\, e^2\, N}{10^3 DkT}\,\mu}\right\} \qquad (3)$$

$$= \frac{2\, e^2}{3DkT}\sqrt{\frac{8\pi\, e^2\, N}{10^3\, DkT}} \times z_A z_B\, kT\, \sqrt{\mu},$$

and on substituting for $e = 4.774 \times 10^{-10}$, $N = 6.06 \times 10^{23}$, $R = 8.315 \times 10^7$ $D = 78.8$ and $T = 298$. This reduces to $1.52\ kT\ z_A z_B \sqrt{\mu}$

Now E_o, the activating energy for a pair of molecules may be regarded as composed of two parts, the potential energy, $1.52\ k\ T\ z_A\ z_B \sqrt{\mu}$ and the kinetic energy E_k, determined by a Maxwell distribution, ie, $E_o = E_k + 1.52\ kT\ z_A\ z_B \sqrt{\mu}$. Those molecules possessing kinetic energy, E_k, in addition to the potential energy, will be capable of reacting. The speed will thus be given by

$$v = k_o\, C_A\, C_B\, e^{-E_k/kT}$$

$$= k_o\, C_A\, C_B\, e^{\frac{-E_o + 1.52\ kT\ z_A z_B \sqrt{\mu}}{kT}}$$

$$= k_o\, C_A\, C_B\, e^{-E_o/kT + 1.52\ z_A z_B \sqrt{\mu}}$$

Comparing this equation with the classical equation $v = k_2\, C_A\, C_B$, we have

$$k_2 = k_o\, e^{-E_o/kT + 1.52\ z_A z_B \sqrt{\mu}}$$

$$\text{and } \ln k_2 = \ln k_o - E_o/kT + 1.52\ z_A z_B \sqrt{\mu}$$

$$\text{or } \log k_2 = \text{constant} + \frac{1.52}{2.303}\, z_A z_A \sqrt{\mu}$$

$$= C + 0.66\ z_A z_B \sqrt{\mu} \qquad (4)$$

The salt effect to be expected on the present theory is thus approximately two-thirds of that given by the Brönsted equation (2). In order to compare these equations [which, although of similar form, are based on different theories of reaction velocity], the results of a number of investigations have been examined by plotting the log. of the classical velocity coefficient against the square root of the ionic strength. The gradient of this curve will be $P\ z_A z_B$. These data are now considered.

Interaction of persulphate and iodide ions.[1]—The reaction is bimolecular, involving the di-valent persulphate and the mono-valent iodide ions.

[1] Price: Z. physik. Chem., **27**, 474 (1898).

Equivalents persulphate	Equivalents iodide	μ	$\sqrt{\mu}$	k	log k
1/30	1/30	0.083	0.288	76	1.881
1/40	1/40	0.062	0.250	66	1.819
1/50	1/50	0.050	0.224	61	1.785
1/60	1/60	0.042	0.204	58	1.763
1/70	1/70	0.036	0.189	53	1.724
1/80	1/80	0.031	0.177	50	1.699
1/40	1/60	0.054	0.233	61	1.785
1/60	1/40	0.050	0.224	62	1.792
1/40	1/80	0.050	0.224	60	1.778
1/80	1/40	0.044	0.209	58	1.763

Observed gradient (Fig. 1) = 1.5; 0.66 $z_A z_B$ = 1.32

Interaction of formate and silver ions.[1] The reaction was found to be termolecular on the lines $2Ag^{\cdot} + HCOO' = 2Ag + CO_2 + H^{\cdot}$ The potential energy possessed by the three ions will be

$$\tfrac{1}{3}\left\{-2z_A^2 - z_B^2 + (2z_A + z_B)^2\right\} \quad \left\{\frac{e^2}{D}\sqrt{\frac{8\pi e^2 N\mu}{10^3 DkT}}\right\}$$

giving the equation

$$\log k = C - 0.66\sqrt{\mu}.$$

Mols formate	mols silver salt	μ	$\sqrt{\mu}$	k	log k
0.100	0.100	0.200	0.458	31.1	1.493
0.050	0.050	0.100	0.316	37.4	1.573
0.025	0.025	0.050	0.224	43.7	1.640
0.100	0.050	0.150	0.387	35.6	1.551
0.050	0.025	0.075	0.274	42.3	1.626
0.050	0.100	0.150	0.387	29.8	1.474
0.025	0.050	0.075	0.274	36.9	1.567

Gradient (Fig. 2) = −0.6; calculated = −0.66

Interaction of hydroxyl and dibromsuccinate ions.[2]—The reaction is bimolecular and may be represented.—

$$(CH\ Br\ COO)_2'' + OH'' \longrightarrow \begin{matrix} C\ Br\ COO'\ (+ H_2O + Br') \\ \| \\ C\ H\ COO' \end{matrix}$$

Mols BNa_2	Mols NaOH	μ	$\mu^{1/2}$	k	log k
0.01222	0.01222	0.0489	0.221	1.51	0.179
0.01727	0.01727	0.0691	0.263	1.64	0.215
0.02473	0.02473	0.0989	0.315	1.85	0.267
0.03109	0.03109	0.1244	0.353	1.85	0.267
0.04504	0.02252	0.1407	0.397	2.19	0.340
0.02815	0.05630	0.1576	0.375	2.19	0.340
0.03753	0.03752	0.1501	0.387	2.07	0.316

Gradient (Fig. 3) = 0.95; 0.66 $z_A z_B$ = 1.32.

[1] Noyes and Cottle: Z. physik. Chem., **27**, 579 (1898).
[2] Holmberg: Z. physik. Chem., **79**, 147 (1912).

The presence of other sodium salts alters the velocity coefficient in accordance with the change in ionic strength, but the presence of potassium or barium ions increases the speed very much more than would be anticipated. Positive ions appear to exert a specific effect on the potential of negative ions and vice versa. This is very noticeable in the reaction between $\alpha\beta$ di-brom-

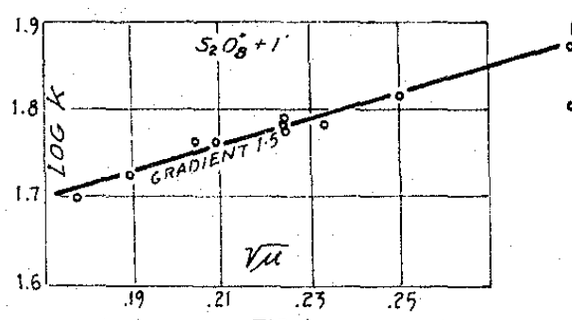


FIG. 1

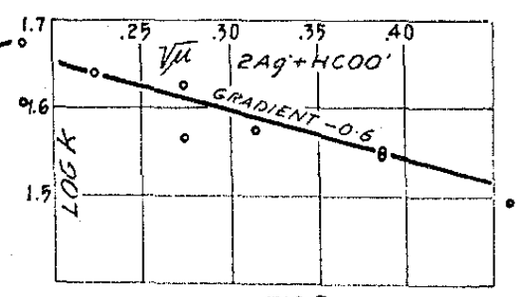


FIG. 2

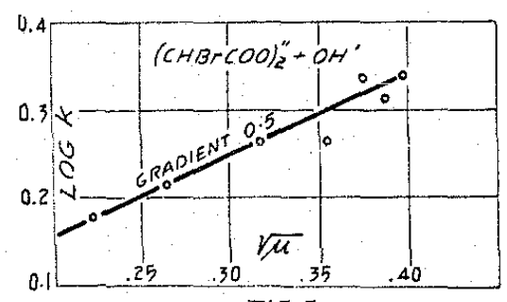


FIG. 3

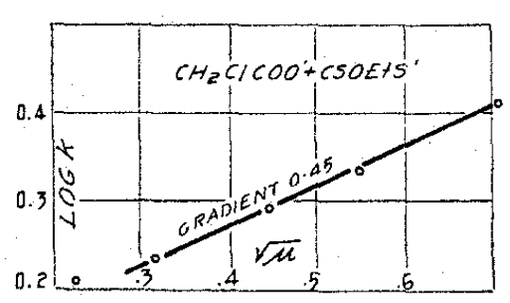


FIG. 4

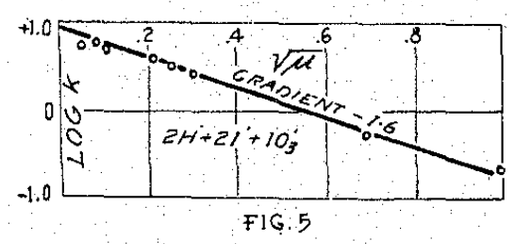


FIG. 5

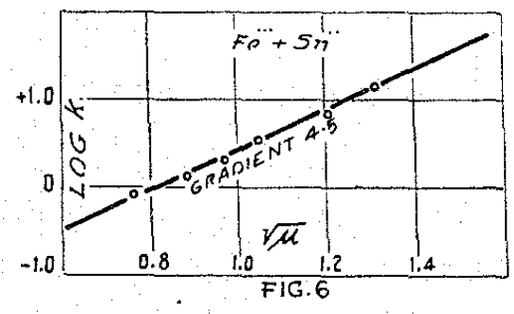


FIG. 6

propionic acid and alkali and that between $\alpha\beta$ di-brom butyric acid and alkali, which involve the anion of the acid and hydroxyl ion[1], and also in the reaction between hydroxyl and the anion of acetyl glycollic acid[2], where the effect of changing the cation is to alter the velocity without, however, changing the gradient of the log k $\sqrt{\mu}$ curve. The gradients of these curves are included in the summarising Table below.

When Brönsted and Livingston's results for the interaction of the ions $CoBr(NH_3)_5^{\cdot\cdot}$ and $Hg^{\cdot\cdot}$ are examined in groups according to the nature of the added salt present, it will be seen from their curve (Fig. 4 in their paper) that the gradient is approximately 3, whilst that of the curve obtained from a study of the interaction of the ions $CoBr(NH_3)_5^{\cdot\cdot}$ and OH' is more nearly -1.4. The authors record the gradients as 4 and -2 respectively.

[1] Holmberg: Z. physik. Chem., **84**, 451 (1913).
[2] Holmberg: Z. physik. Chem., **88**, 385 (1914).

Interaction of iodide and iodate[1].—The reaction between $H^{\cdot}$, I', and IO_3' ions is quinquemolecular following the equation

$$v = k\,[IO'_3]\,[I']^2\,[H]^{\cdot 2}.$$

The potential energy possessed by these ions will be

$$\tfrac{1}{3}\left\{-z_A^2 - 2z_B^2 - 2z_C^2 + (z_A + 2z_B + 2z_C)^2\right\}\ \left\{\frac{e^2}{D}\sqrt{\frac{8\pi\, e^2\, N\mu}{10^3\, DkT}}\right\}$$

giving the equation

$$\log k = C - 1.32\sqrt{\mu}$$

Increase of μ should therefore decrease k, as is observed. As the velocity coefficient does not change appreciably during the fractional change studied, the ionic strength has been calculated from the initial concentrations of the reagents.

Expt. No.	μ	$\sqrt{\mu}$	k (= x_2)	log k
25	0.0024	0.049	5.1	0.708
26	0.00606	0.078	5.8	0.763
27	0.01298	0.114	4.8	0.681
28	0.0429	0.207	3.7	0.568
29	0.0625	0.250	3.1	0.491
30	0.0865	0.294	2.6	0.415
31	0.471	0.686	0.53	$\bar{1}$.724
32	0.972	0.986	0.22	$\bar{1}$.342
33	3.18	1.780	0.069	$\bar{2}$.839
34	6.36	2.520	0.029	$\bar{2}$.462

Gradient (Fig. 5) = −1.6

The Brönsted theory in this case gives

$$v = k_o\, C^2_{H^{\cdot}}\, C^2_{I'}\, C_{IO^{\cdot}_3}\, \frac{f^2_{H^{\cdot}}\, f^2_{I'}\, f_{IO_3'}}{f_x} = k_o\, C^2_{H^{\cdot}}\, C_{IO_3'}\, \frac{f_I^5}{f_I},$$

where f_I is the activity coefficient of a univalent ion, and hence

$$\log k = \log k_o + 4\log f_I$$
$$= \log k_o - 4 \times 0.50\, z_I^2\sqrt{\mu} = \log k_o - 2.0\sqrt{\mu}.$$

Interaction of ferric and stannous ions[2].—This reaction gives a termolecular constant, $2\,Fe^{\cdot\cdot\cdot} + Sn^{\cdot\cdot} \longrightarrow 2\,Fe^{\cdot\cdot} + Sn^{\cdot\cdot\cdot\cdot}$, but in a concentrated salt solution gives a bimolecular constant. As the ions are multivalent, the reaction would be expected to exhibit a large salt effect and the velocity coefficient will be very sensitive to changes in the ionic strength. If the stannic chloride formed be regarded as giving rise to only a slight concentration of stannic ions, which is suggested by its slow hydrolysis in water there will be over 100% change in the ionic strength as the reaction proceeds and no constant velocity coefficient would be expected. In excess of salt

[1] Abel and Stadler: Z. physik. Chem., **122**, 49 (1926).
[2] Timofeev, Muchin and Gurewitsch: Z. physik. Chem., **115**, 161 (1925).
[3] Kowalevsky: Z. anorg. Chem., **23**, 1 (1900).

Reaction	Observed Gradient	Brönsted Calc.	Brönsted Error	Equation 4 Calc.	Equation 4 Error	P
$S_2O_8'' + I'$	1.5	2.0	+0.5	1.32	−0.18	0.75
$_2Ag^{\cdot} + HCOO'$	−0.6	−1.0	+0.4	−0.66	+0.06	0.6
$C . HBrCOO'$						
$C . HBrCOO' + OH'$	0.95	2.0	+1.05	1.32	+0.37	0.47
$CH_2Br . CHBr . COO' + OH'$	0.5	1.0	+0.5	0.66	+0.16	0.5
$C_2H_5Br . CHBr . COO' + OH'$	0.4	1.0	+0.6	0.66	+0.24	0.4
$CoBr(NH_3)_5^{\cdot\cdot} + OH'$	−1.4	−2.0	+0.6	−1.32	−0.08	0.7
$CoBr(NH_3)_5^{\cdot\cdot} + Hg^{\cdot\cdot}$	3.0	4.0	+1.0	2.64	−0.36	0.75
$CH_2ClCOO' + CSOEtS'$*	0.45	1.0	+0.55	0.66	+0.21	0.45
$_2H^{\cdot} + _2I' + IO_3'$	−1.6	−2.0	+0.4	−1.32	−0.28	0.8
$Fe^{\cdot\cdot\cdot} + Sn^{\cdot\cdot}$	4.5	6.0	+1.5	3.96	−0.54	0.75
		Mean	+0.71		−0.04	0.62 ± .13

*Holmbeg. Z. physik. Chem., **88**, 385 (1918).

where the ionic strength is practically constant, a constant bimolecular velocity coefficient is obtained, suggesting that the reaction is always bimolecular. It is noteworthy that the bimolecular velocity coefficients decrease as the reaction proceeds in accordance with the decrease in the ionic strength. In the following Table the initial values of k_2 have been taken (corresponding to a 10—20% change) and the square root of the ionic strength calculated from the initial concentration. If the reaction is bimolecular the gradient of the log k $-$ $\sqrt{\mu}$ curve should be 0.66 $z_A z_B$ = 3.96.

$FeCl_3$ = 0.0625M; $SnCl_2$ = 0.0625 /2 M.

NaCl mols	μ	$\sqrt{\mu}$	k_2	log k_2
0.15625	0.6237	0.790	0.773	$\bar{1}$.888
0.3125	0.7800	0.883	1.30	0.114
0.46875	0.9362	0.967	2.14	0.330
0.6250	1.092	1.04	3.47	0.540
0.9375	1.405	1.20	7.17	0.856
1.250	1.717	1.31	14.3	1.155
2.500	2.967	1.72	17.4	1.240
2.923	3.390	1.84	33.5	1.525

Gradient (Fig. 6) = 4.5

For comparison the observed and calculated gradients of the various log k $-$ $\sqrt{\mu}$ curves have been collected. In the last column is the value of P calculated from the observed gradient and the equation log k = C + P $z_A z_B$ $\sqrt{\mu}$. Differences between the observed and calculated gradients are recorded as + if the theory has over-predicted.

The experimental results are thus in good agreement with the hypothesis that the total electrical potential energy of the ions contributes to the energy of activation of an ionic reaction.

Summary

1. An equation for the rate of interaction of ions is developed in which the potential energy possessed by the ions in virtue of their charges is regarded as contributing to the critical increment of the reaction. The potential energy of the ions is evaluated from the Debye-Hückel theory and the equation

$$\log k = C + 0.66\, z_A z_B \sqrt{\mu}$$

derived, k being the classical velocity coefficient, z_A and z_B the valences of the ions and the ionic strength.

2. The equation has been tested on reactions of various ionic types by determining P in the equation log k = C + P $z_A z_B$ $\sqrt{\mu}$ by a graphical method. The average value of P is 0.62 $\pm$ .13.

University College of North Wales,
Bangor
May 2, 1927.

THE RELATION OF VAPOR PRESSURE TO PARTICLE SIZE*

BY S. LAWRENCE BIGELOW AND H. M. TRIMBLE**

The Thomson Equation

It has been shown on theoretical grounds that, if a liquid is broken up into small droplets, or if it is held in pores or other similar spaces which are of capillary dimensions, its vapor pressure is a function of the curvature of the surface[1] which is presented to the vapor phase. The relation between these quantities is set forth in the well-known Thomson equation;

$$\log_e \frac{P}{P_o} = \frac{2\gamma M}{rs\,RT}, \qquad (1)$$

where P and P_o are the vapor pressures of a given liquid, respectively, at a surface whose radius of curvature is r and at a plane surface; γ is the surface tension of the liquid; T is the temperature on the absolute scale; M is its molecular weight; s is its density; and R is the gas constant.

The development of the Thomson equation is well known, and need not be repeated here. A typical treatment is given by Patrick.[2] It is an ideal expression, based upon fundamental thermodynamic principles. It is universally accepted, largely because of the weight of authority inherent in its source. But we have failed to find in the literature either any quantitative experimental confirmation of its predictions or any thorough study of its applicability and limitations. All the experimental evidence for it is of a purely qualitative nature; and, even as such, this evidence is not always clear and convincing.

Three assumptions are made in the development of the Thomson equation, namely:

A. The substance in the molecularly dispersed phase obeys the ideal gas laws.

B. The surface tension of the substance is independent of its degree of subdivision.

C. The density of the substance is independent of its degree of subdivision.

We have never yet found anything conforming exactly to the ideal gas laws, and so assumption A is assuming too much for the molecularly disperse phase. For particles so large that the vapor pressure does not differ appreciably from that at a plane surface, only a negligible error is introduced; but when the molecular dimensions are approached the error will be large.

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*Contribution from the Chemistry Laboratory of the University of Michigan.

**The work presented in this paper is taken from a dissertation presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

[1] The curvature of a surface is equal to the reciprocal of its radius of curvature.

[2] "Treatise on Physical Chemistry." Edited by H. S. Taylor. Vol. II, p. 1290 (1925).

As to the second assumption, (B); it seems certain that the surface tension of a liquid must vary with its degree of dispersion. Sir William Thomson,[1] on the basis of the Laplace theory of surface tension, considered it probable that the surface tension of water at a meniscus whose radius of curvature is less than 0.0012 millimeter is no longer independent of the curvature of the surface, but his reasoning is not given. He cautions against using the equation for very small capillaries.

Freundlich,[2] upon a similar basis, reached the conclusion that the surface tension of a liquid in the form of small droplets must be less than that at larger surfaces. He believed this true for droplets whose radius is of the order of magnitude of the range of molecular action; but admitted that this does not give a satisfactory basis for the calculation of their size.

Patrick and Eberman[3] found reason to believe, from studies of selective adsorption, that a liquid has a much higher surface tension than ordinarily if its surface is exceedingly concave, as it is when held in a very small capillary space. Other evidence is found in work by Patrick, Preston and Owens.[4] They found that a gas will condense (presumably to a liquid) in the capillary spaces which are found in silica gel, at temperatures above its critical temperatue. In other cases it was found that gases condensed in such capillary spaces at pressures which were always below the saturation pressures for these gases in contact with their liquid phases. They found, too, that adsorption takes place from solution above the critical solution temperature. It follows from these results that the critical temperature for a liquid in a capillary is higher than that for the liquid in bulk. If this is true, then the surface tension must also be higher, because the temperature—surface tension curve, which is nearly linear, cuts the temperature axis at or near the critical temperature.

Harkins, Davies and Clark,[5] reasoning from the theory that molecules are oriented at interfaces, concluded that the surface tension of a liquid must be a function of the curvature of its surface. At a plane surface, or at one which is not greatly curved, the molecule can fit the surface; and under such conditions the normal surface tension is displayed. At a surface which is sufficiently curved, however, the molecules will be differently arranged. At such surfaces, then, the forces between them are modified, and a different surface tension should result.

The third assumption, (C), is also open to question. E. A. Fisher[6] found that there is reason to believe that the density of water in a capillary pore is less than that of water in bulk. When a film is adsorbed upon a solid surface, he reasoned, it is held there by adhesive forces of great magnitude. If a very small capillary is partially filled with water the action of the forces which are

[1] Proc. Roy. Soc. Edinburgh, 7, 63 (1870).
[2] H. Freundlich: "Kapillarchemie," 63 (1922).
[3] W. A. Patrick and N. F. Eberman: J. Phys. Chem., 29, 227 (1925).
[4] W. A. Patrick, W. C. Preston and A. E. Owens: J. Phys. Chem., 29, 421 (1925).
[5] W. D. Harkins, E. C. H. Davies and G. L. Clark: J. Am. Chem. Soc., 39, 592, 595 (1917).
[6] E. A. Fisher: J. Phys. Chem., 28, 363-4 (1924).

active in its surface will tend to stretch the water in it. As a result it will be put under a tension, and its density will be reduced in proportion. He gives about three microns as the diameter of a capillary in which this effect would probably begin to be noticeable.

The assumptions upon which the Thomson equation is based are, then, somewhat unreliable. Like the equation itself, they stand in need of experimental investigation. In the absence of actual data it is impossible to make an exact statement, but the consensus of opinion seems to be that assumptions B and C fail to hold for a surface whose radius of curvature is of the order of magnitude of one micron, or less. This is approximately the limit of microscopic visibility. The Thomson equation is, then, from this point of view, applicable only to bodies which are experimentally measurable.

Calculations from the Equation

Calculation from the Thomson equation shows that the vapor pressure of a liquid at a curved surface differs from that at a plane surface by an amount which is quite inappreciable, even for droplets which are comparatively small. The values of the increase in vapor pressure, $P - P_o$, and of the relative increase in vapor pressure, $(P - P_o)/P_o$, as calculated for droplets of water and mercury of various sizes are given in Table I. Here P is the vapor pressure of the droplet, and P_o is that at a plane surface. Thus the Thomson equation leads to the conclusion that the vapor pressure of a droplet of water or mercury exceeds that of a very large body of the same substance by one thousandth

TABLE I

Calculations from the Thomson Equation

Radius of droplet in centimeters	For Water		For Mercury	
	$P - P_o$ mm. Hg.	$\frac{P - P_o}{P_o}$	$P - P_o$ mm. Hg.	$\frac{P - P_o}{P_o}$
1.0	0.0_52	0.0_61	0.0_97	0.0_65
0.1	0.0_42	0.0_51	0.0_87	0.0_55
0.01	0.0_32	0.0_41	0.0_77	0.0_45
0.0_21	0.0_22	0.0_31	0.0_67	0.0_35
0.0_31	0.019	0.0_21	0.0_57	0.0_25
0.0_41	0.189	0.011	0.047	0.058
0.0_51	1.99	0.113	0.0399	0.764
0.0_61	33.84	1.930	0.036	28.094
0.0_71	818,710.	46,569.	5.6×10^{22}	4.35×10^{25}

of the latter value only when it has a radius of about one micron, i.e. 0.0001 centimeter. For surfaces of greater curvature the calculated effect increases, and becomes enormous for a droplet whose radius approaches the molecular dimensions.

The Thompson equation may be put in the form:

$$\log_e \frac{P}{P_o} = \frac{2\gamma M}{s\ RT} \cdot \frac{1}{r} = \frac{K}{r} \tag{2}$$

where K is a constant for a given liquid at a given temperature. Under

ordinary conditions K will always be very small, because the large value which must be assigned to R, the gas constant, will far outweigh the effect of the values of M, γ and s. We have calculated the values of K for eighty representative liquids at temperatures close to 20° C., and find them to vary from 0.000,000,076 for methyl alcohol, a liquid of low molecular weight and low surface tension; to 0.000,000,56 for mercury, whose molecular weight and surface tension are the highest known. The average value of this constant for all these liquids is 0.000,000,25. It seems that its value for any liquid will lie between these limits. We may, then, say that K for any liquid at about this temperature is, for practical purposes, a constant, of the order of magnitude of 0.000,000,3. It thus appears that the vapor pressure of any liquid at a curved surface, as calculated from the Thomson equation, will differ from that at a plane surface by as much as one thousandth of the latter value, only when its radius of curvature is of the order of magnitude of one micron.

Theoretically, then, the Thomson equation should be applicable to surfaces whose radii of curvature are one micron or more in length. This lower limit is set by the probable limit of validity of the assumptions upon which the equation is based. A glance at Table I shows that the effect, in terms of vapor pressure, as predicted from the equation is very small for any droplet of water or of mercury such as would ordinarily be met with; so small, indeed, that it seems doubtful whether it could be effective at all. These considerations lead us to the conclusion that the limits within which the Thomson equation is actually applicable are probably very narrow.

The Thomson equation, with suitable modifications, holds quite as well, theoretically, for the vapor pressures of solid particles and for the solution pressures of solid or liquid particles as for the vapor pressures of liquid bodies.

Previous Experiments

The more important evidence for the Thomson equation may be briefly summarized. Numerous investigators have found that substances have greater solubilities when finely divided. A very pretty qualitative demonstration of this fact is due to Kenrick.[1] Ostwald[2] found that finely divided mercuric oxide is more soluble in normal solutions of potassium bromide and sodium thiosulfate than is coarser material. He got similar results for the solubilities of various salts in water. Hulett[3] found that the solubility of gypsum and barium sulfate in water is greater when finely divided, and established the fact that, for particles of either substance larger than about two microns in diameter, the solubility is no longer a function of particle size. Both Ostwald and Hulett found that large particles grow slowly at the expense of very small ones when both are in contact with the same solution. No attempt was made to determine the solubility of the smaller particles as a function of particle size; so the experiments do not furnish any quantitative confirmation of the Thomson equation.

[1] F. B. Kenrick: J. Phys. Chem., **16**, 516 (1912).
[2] Wilhelm Ostwald: Z. physik. Chem., **18**, 159 (1895); **34**, 495 (1900).
[3] G. A. Hulett: Z. physik. Chem., **37**, 385 (1901); **47**, 357 (1904).

A number of investigators[1] have reported that larger crystalline bodies grow, by sublimation, at the expense of smaller ones. In all of these cases the details as to the conditions which prevailed during the experiments are meager or lacking. It seems to us probable that the changes noted were due to temperature differences rather than to differences in vapor pressure between the particles studied.

Ostwald[2] and McKeehan[3] believed that, in certain systems, small droplets of liquids distil over to larger ones. We shall discuss these experiments in detail.

Other evidences of this sort might be cited, but the above will serve to indicate the nature and quality of the work which has been done.

Experimental

Sulfur

Ostwald[4], after discussing the difference in vapor pressure which exists between the surfaces of two droplets of unequal size, says:

"One can demonstrate the existence of such a difference by putting a liquid, which must not be too volatile, in a tube, evacuating and sealing it, and then producing a deposit of droplets on its walls. Now if the tube is put aside it will be found after some time that the droplets which were larger than the others at first have surrounded themselves with cleared spaces, showing that the neighboring smaller droplets have distilled over to these larger ones. A suitable material for this experiment is sulfur, which deposits from the vapor phase in the liquid form."

We repeated this experiment of Ostwald's.

Test tubes of soft glass were prepared by washing them with distilled water, allowing them to stand for 24 hours or longer filled with fresh aqua regia, steaming them out and drying them in an oven. The tubes were drawn out to provide a narrow neck for sealing off, and were then allowed to stay in the hot air bath until wanted. Our experience showed that tubes so prepared were satisfactorily clean.

Sulfur was at first prepared by distilling from a small retort, the distillate being run into conductivity water. After it had hardened it was dried and pulverized. Later, sulfur was prepared by recrystallizing from carefully purified carbon tetrachloride and drying in the hot air-bath for some hours.

A few fragments of sulfur were introduced into a tube which was then evacuated to some desired pressure and sealed. Gentle heating caused a deposit of sulfur droplets to form upon its walls.

Sulfur deposits from the vapor phase in liquid droplets which vary in size from those which can just be seen with a microscope to those which have

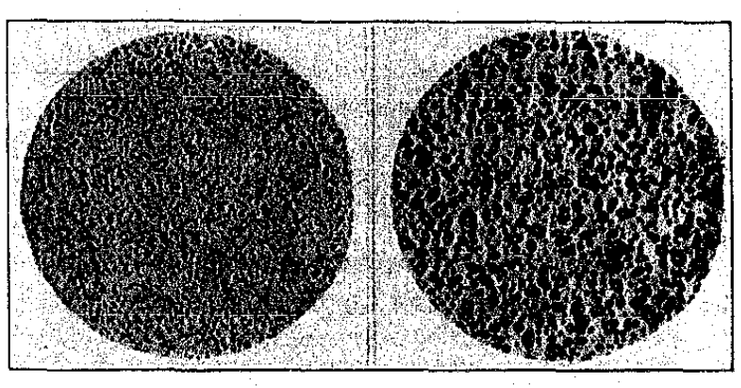
[1] W. D. Herman: Chem. Centralblatt, **1874**, 3; J. Lawrence Smith: Dingler's Polytechn. J., **121**, 402 (1874); H. Freiherr Jüptner von Jonstorff: Ber., **10**, 866 (1877); O. D. von Engeln: Am. J. Sci., (4) **40**, 461 (1915); R. S. Willows and E. Hatschek: "Surface Tension and Surface Energy," 30 (1923).

[2] Wilhelm Ostwald: "Grundriss der allgem. Chemie," 96.

[3] L. W. McKeehan: Phys. Rev., (2) **8**, 142-8 (1916).

[4] Loc. cit.

a diameter of a millimeter or more. The nature of the deposit varies with the stage at which the deposition is stopped. Microphotographs of characteristic deposits are shown in Fig. 1. The droplets in light deposits are small, circular in cross section, and rather widely spaced. If the condensation of sulfur is slow and regular these droplets grow uniformly. After certain size is reached a process of coalescence sets in:—some droplets run together. An early stage in this process may be seen in A of Fig. 1. As condensation goes on, running together becomes more active; and it not uncommonly persists for some time after deposition of sulfur has been stopped. Droplet systems which have come to equilibrium, so far as this change is concerned, are very often like that shown in B; but it is possible to get systems whose droplets, though comparatively large, are very regular. After a time some of the larger droplets turn crystalline. A few which have so changed may be seen in B of Fig. 1.



A B

FIG. 1
Deposit of sulfur droplets
× 20

They are opaque, whereas droplets which are still liquid show axial spots of light. It seldom happens that more than a few droplets turn crystalline. The transformation is quite random, and apparently accidental. Constancy of temperature has a stablizing effect, tending to prevent crystallization, and this effect is greater the higher the temperature.

The form of these droplets is significant. Some sulfur was deposited upon a small glass rod and examined under the microscope. As seen in vertical cross-section, the line of sight being tangent to the surface upon which they rested, the droplets were seen to be spread upon it, showing much flattened contours of the form which droplets of any liquid take when placed upon a surface which it wets. The deposit of sulfur upon glass is analogous to a thick film of oil upon water. We believe that the droplets of sulfur exist in more or less stable equilibrium with a thin film of liquid sulfur which covers all the rest of the glass surface and connects them all together, and that the existence of this film on the glass accounts for the manner in which the droplets run together.

We found that when these tubes with their droplet systems were set aside, cleared spaces formed just as described by Ostwald; but the central bodies to which distillation takes place are crystalline, not liquid.

Salomon[1] was apparently the first to observe the distillation of sulfur droplets to crystals. He found that, under the conditions of his experiments, crystals of nacreous sulfur are formed. Whitaker[2] describes, and shows by means of microphotographs, the formation of solid bodies of five types at the expense of sulfur droplets. These are: solidified droplets of indefinite form, octahedrons, nacreous plates, hexagonal plates and curved hair-like crystals. These forms were found with light deposits of fine droplets at atmospheric pressure. We have repeated this portion of his work with very similar results.

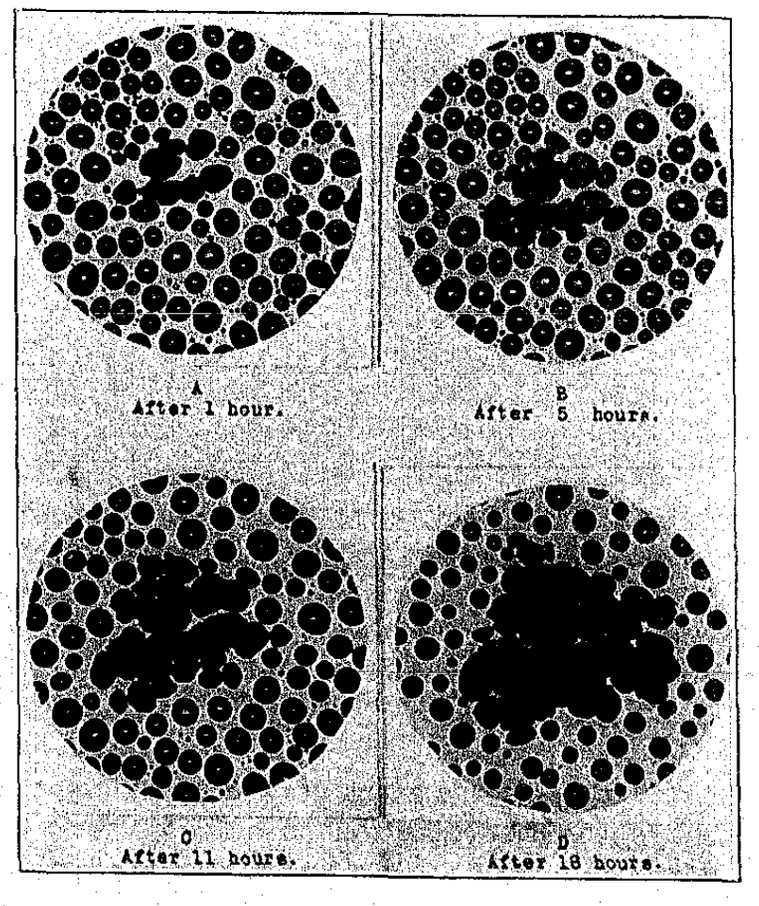


FIG. 2
Distillation of sulfur droplets to crystals. Room temperature.
× 50

The changes in a characteristic experiment of ours are shown in the microphotographs of Figs. 2 and 3. The pressure in this tube was 0.001 millimeter of mercury. It was kept at the temperature of the room. The deposit, which was very uniform, consisted of droplets which ranged from about 2 or 3 to 80 microns in diameter. Immediately after it was formed, the tube was brought under the microscope, and all parts of the deposit were examined. At the end of ten minutes a few widely scattered droplets had solidified. Our method was to select a small area for close study. We pasted a bit of paper with a hole in it on the tube in such a way that the chosen area was visible

[1] W. Salomon: Z. Kryst. Min., **30**, 605 (1899).
[2] H. Whitaker: J. Phys. Chem., **29**, 399 (1925).

through the hole. We found it convenient to refer to such a group of droplets as a system. In the system illustrated by the figures the droplet which is represented by the largest unit of the crystal aggregate shown in A was first to change over. The change then spread to neighboring droplets until the condition shown in photograph A was reached at the end of an hour. Thereafter the system was photographed at the intervals indicated. For more than ten hours the visible change consisted in the growth of the crystal aggregate by inclusion of more droplets. This change, due to coalescence, was at an end after 24 hours.

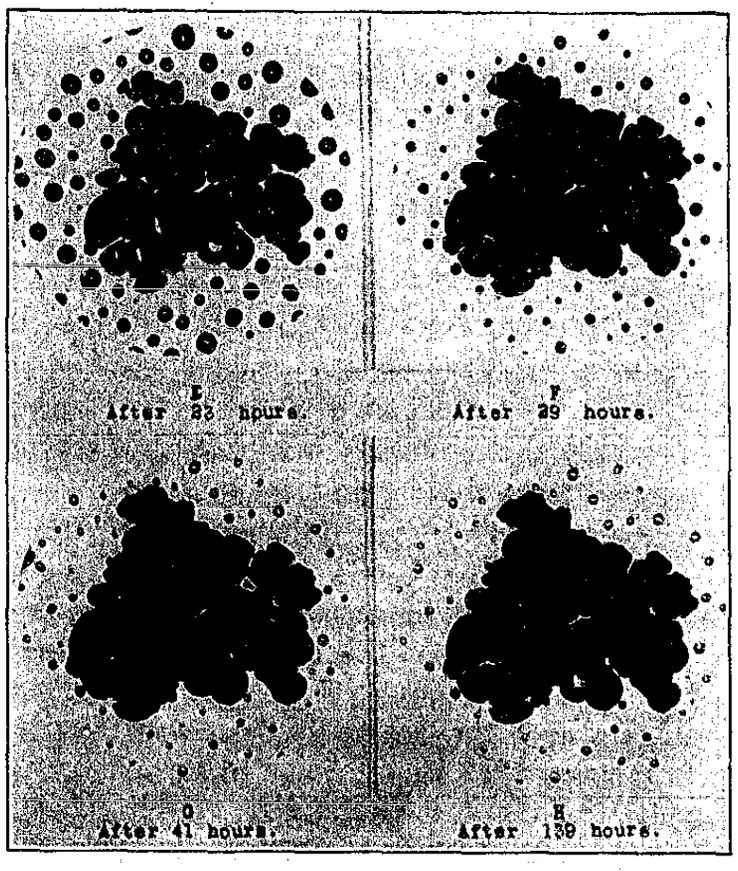


FIG. 3
Distillation of sulfur droplets to crystals, continued. Room temperature.
× 50

Distillation from the droplets to the crystalline aggregate was going on all the time, as is shown by the growth of the aggregate, but its effect in decreasing the sizes of droplets was definitely obvious only after 11 hours. Measurements of various droplets in succeeding photographs, beginning with photograph C, showed that all of them decreased in dimater at a rate which was roughly proportional to their respective sizes, so far as could be determined, regardless of size or position. After about thirty hours this decrease in diameter was at an end, and the further change consisted in the flattening of the droplets, as shown in F and G. At the end of four days more the condition shown in H was reached. The tube was kept for a month longer, but no further change was observed.

The distance across which distillation takes place from droplets to crystals is of interest. Our experiments indicate that it is definitely limited for given conditions. It was not possible to cover, in a single photograph, at this magnification, the whole area over which the change took place. Observation with the microscope showed that it was only a little larger than the area shown in the series of photographs after eighteen hours. It gradually extended until, after 41 hours it covered a roughly circular area with center at the middle of the crystal aggregate and radius about four millimeters. It was then encroaching upon the areas which were distilling to other centers. This, however, was about the limit which was reached, even after a month.

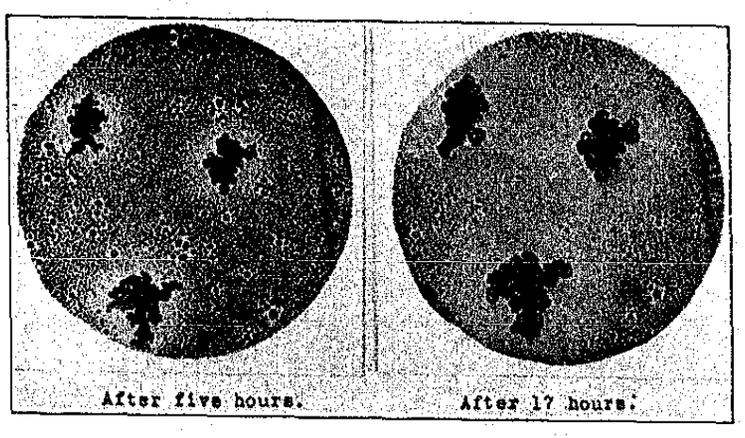


FIG. 4
Distillation of sulfur droplets to crystals. Room temperature.
× 20

In other cases we found no obvious coalescence and the droplets distilled completely away, leaving no trace. The changes in a typical experiment of this sort, again at room temperature and 0.001 millimeter pressure, are shown in Fig. 4. Even after a week the cleared spaces about the crystalling aggregates were but little larger than those shown in the photograph which was taken after the expiration of seventeen hours.

It is noteworthy that, in a number of instances in this experiment, larger and smaller droplets were found very close together; yet no distillation took place from the latter to the former. Such a group is found at about the position which is 4 o'clock on the dial of a watch. Another is close to 3 o'clock, and yet another is between 8 and 9 o'clock. It seems that the distillation from droplets to crystals, with sulfur, is very much more rapid than the distillation between droplets of different sizes.

The spreading of the crystal state from those droplets which are first transformed to their immediate neighbors is evidently closely related to the running together of droplets which has been mentioned; for the droplet which undergoes the change is usually jerked toward the crystal aggregate which is already in existence at the instant when it is transformed. This feature of the change was observed many times under the microscope during our study of these systems. It was found sometimes, too, that a tiny tongue of solid sulfur connected the newly converted droplet with the original crystalline

mass. Several istances may be seen in A and B of Fig. 2. We believe that the crystalline state spreads to new droplets through the crystallization of a film of sulfur which lies on the glass between the droplets and the crystalline aggregates, and that the spreading ends when this film disappears by distillation. The running together of droplets, the spreading of crystallization and its cessation furnish very good evidence for the existence of such a film.

The changes described took place in the same manner, and at about the same rate at different pressures up to 12 millimeters of mercury. The presence of air at atmospheric pressure decreases the rate of distillation from droplets to crystals very greatly. So far as could be ascertained, constancy of temperature is not essential for the satisfactory progress of this distillation. Under the most favorable conditions, however, the distillation is very slow at low temperatures.

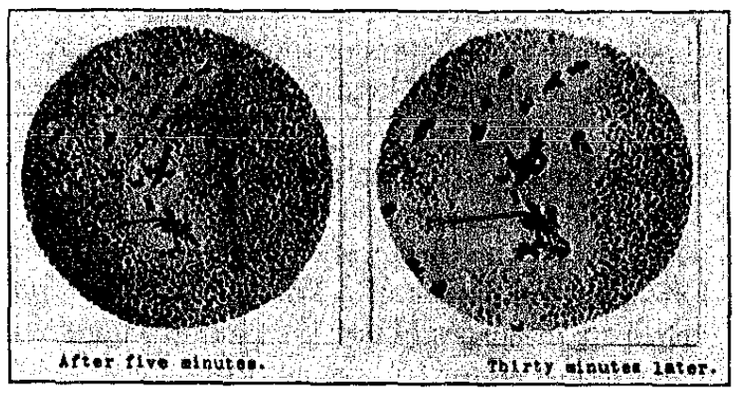


FIG. 5
Distillation of sulfur droplets to crystals. 75°C.
× 40

Experiments were tried at higher temperatures also. It was found that when evacuated tubes were placed in a hot air bath at approximately 75° C. the sulfur droplets in them distilled rather rapidly from place to place, due to temperature differences, thus preventing the study of the distillation from droplets to crystals which is produced by vapor pressure differences.

Experiments at higher temperatures with tubes which contained air at atmospheric pressure were more successful. In these experiments the tubes were inserted in the hot air bath for five minutes, removed for examination and photographing and then again returned to the bath. Microphotographs from one such experiment are shown in Fig. 5. Apart from the more rapid clearing away of droplets, which was obvious, it is noteworthy that spreading of the crystalline state to new droplets was practically eliminated.

We next suspended the tubes with their systems in the vapors of boiling chloroform, carbon tetrachloride, and toluene, respectively, in large test tubes, and observed them where they were, using a low-powered microscope mounted upon a cathetometer. This eliminated the necessity of removing the tubes for examination. There was no distillation due to temperature differences. We found, as anyone would expect, that the changes are more rapid and more extensive the higher the temperature and the lower the pressure.

There was, however, no regularity either in the rate in which given droplets decreased in size or in the rate at which cleared spaces extended about growing crystals. This is, no doubt, due to the fact that not one, but always several crystals were growing simultaneously, and the changes were correspondingly complex.

All this, however, failed to settle the question whether large liquid droplets of sulfur grow at the expense of smaller ones by distillation, or not. We found that if a tube was put into the vapor of a boiling liquid in one of our "test tube" thermostats at 60° C. or higher, immediately after a deposit had been formed in it and before any of its droplets had a chance to turn crystalline; all its droplets remained liquid indefinitely. Under these conditions, no cleared spaces were found to form in experiments which lasted as long as three weeks.

Crystals such as formed in many experiments, when melted, give droplets which are sometimes three millimeters or more in diameter, and these droplets also remain liquid indefinitely if kept at a constant temperature of 60° C. or higher.

Systems were now prepared by melting such crystals, and then quickly causing a little sulfur to deposit around the droplet which had just formed. The tubes were then put in the thermostat, generally in the vapor of boiling chloroform, and watched by means of a low power microscope. In no case did we find any clearing of spaces about the large droplets, or any other indication of a distillation of sulfur from small droplets to large ones, even in experiments in which the observations were continued through three weeks. In these experiments the large droplets were .3 to .7; and the small ones were 0.001 to 0.030 millimeters in diameter.

Since we have never found distillation from small droplets of liquid sulfur to large ones under any conditions, it seems fairly certain that Ostwald was in error in believing that he had observed it. What he saw was undoubtedly the distillation from droplets to crystals. The getting of data upon the relation of vapor pressure to particle size is manifestly impossible with these systems.

Phosphorus and other Substances

A number of experiments which we have performed show that yellow phosphorus behaves, in general, in exactly the same manner as does sulfur. It deposits from the vapor phase in droplets; these droplets coalesce by running together; some of them turn crystalline after a time, and when they do the crystalline state spreads to neighboring droplets; and droplets distil to crystals or to crystalline aggregates. Some experiments which we performed in a thermostat at 61° C. showed that, under these conditions, small droplets do not distil over to the larger ones in the course of a week. We believe that liquid phosphorus, like liquid sulfur, wets glass; and that when deposited on glass its droplets have practically the same vapor pressure regardless of size.

We have carried out numerous experiments with water, ether, carbon disulfide, chloroform, carbon tetrachloride, toluene, nitrobenzene, anilin,

and acetic acid deposited upon glass. When the tubes containing such deposits are exposed to the air of the room distillation due to temperature differences always takes place. When, however, they are kept in a carefully regulated thermostat this distillation ceases. Running together of the droplets occurs readily and irregularly. We were unable to obtain anything like the clear-cut "systems" which we had with sulfur and phosphorus. These experiments did not lead us to anything new; but they certainly did not furnish any evidence that vapor pressure is a function of particle size for droplets of these liquids upon glass.

We conclude, contrary to the generally accepted belief, that droplets of liquids which wet glass, when deposited upon it, do not show the distillation from small droplets to large which is predicted from the Thomson equation.

Mercury

McKeehan[1] found that small droplets of mercury distil to large ones provided the space above them is enclosed so that it becomes saturated with mercury vapor.

Mercury droplets upon glass are practically spherical in form, provided they are less than about one millimeter in diameter. The deposits show no tendency to run together. So great is the inertia of the droplets, due to the high density of mercury, that they are rather easily displaced by jarring unless they are very small. When so brought into contact, they of course, unite; but the process is not at all like that which found is with liquids which wet glass. either in its progress or in the nature of the bodies which result from the union. Only reasonable care in handling is sufficient to avoid moving the droplets if none of them are larger than one millimeter in diameter.

The mercury which we used in these experiments was given a preliminary purification by dropping it through a long tube filled with 10% nitric acid. This product was then twice distilled by the method of Hulett[2], aspirating air through it at a pressure of 25 millimeters of mercury. When wanted for use it was drawn from beneath the surface by means of the device commonly employed in a wash-bottle. That which first came from the delivery tube was always rejected to avoid contaminations.

Preliminary experiments showed that the droplets of a deposit formed from the vapor phase upon the walls of a tube are either uniform in size, or show a uniform graduation from large to small as the distance from the place where the mercury is distilled increases. In either case there is little change in such deposits over a period of a week or more. What is needed for the experiment is a system in which large and small droplets lie very close together. After some trials we worked out the following method by which such systems may be prepared. A small droplet of mercury is introduced into one of the prepared tubes, which is then evacuated and sealed. The tube is then immediately reversed so that the mercury in it is brought in contact with the hot end. It distills with such violence that it is disrupted into small particles

[1] Loc. cit.

[2] G. A. Hulett: Phys. Rev., (1) 21, 388 (1905).

which fly about in the tube. Where these particles strike the walls they, adhere. In their flight they emit mercury vapor, which then deposits in fine droplets. It is usually possible to find in a tube a few systems in which small droplets lie very close to others many times their size, after this process.

In the first experiments the tubes were suspended in the air of the room between observations. Fig. 6 shows the changes which took place in one ex-

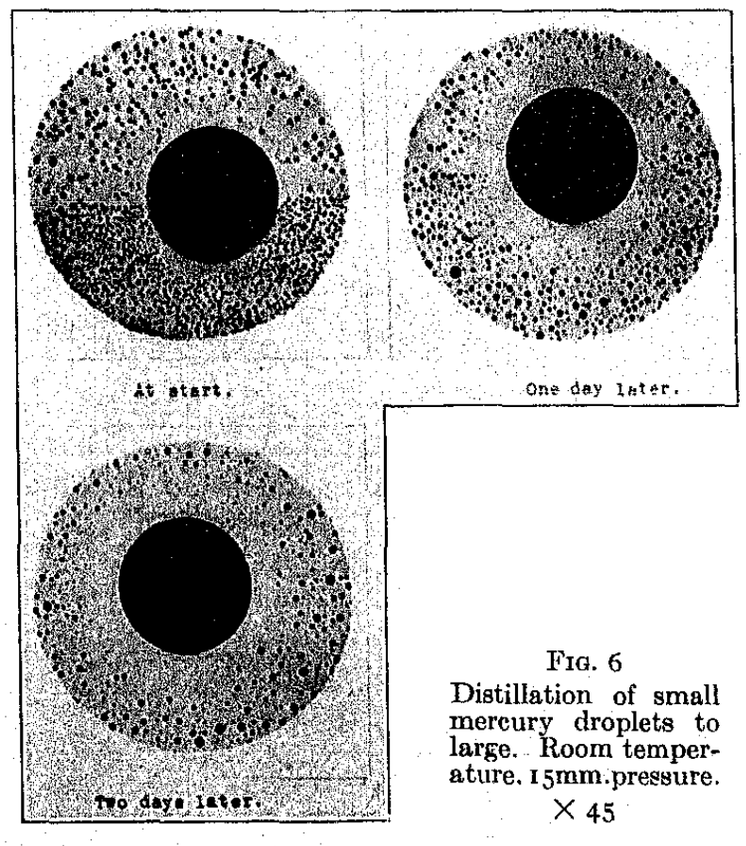


FIG. 6
Distillation of small mercury droplets to large. Room temperature. 15mm. pressure.
× 45

periment, which was typical of very many. The large droplet had a diameter of about 300 microns. At the end of 24 hours, as may be seen, the droplets to a distance of about 0.1 millimeter from the large one had decreased in size, and many of those which were closest had quite disappeared. It is noteworthy that beyond this distance the larger ones among the small droplets had grown at the expense of those which were still smaller. At the end of another 24 hours the clearing away of small droplets around the larger one was more nearly complete, though the space affected was but little greater. The closer small droplets which had grown during the first 24 hour period had decreased somewhat at the end of the second. Those which lay still farther out, however, had continued to grow. The next microphotograph, taken after another 24 hours, showed very little further change. After this time the process was apparently at an end, and observations were discontinued after a week.

The tube in the experiment just described was sealed at a pressure of 15 millimeters of mercury. Although there was some irregularity in the rate of distillation, in a number of experiments at lower pressures the clearing away of small droplets was found to be more rapid and more exten-

sive the lower the pressure. In every case it was found that the larger droplets among the small ones tend to grow at the expense of their smaller neighbors. At the lowest pressure, 0.001 millimeter of mercury, the cleared space extended to a distance of about 0.2 millimeters from the large droplet at the end of two days. In general, the clearing away of droplets was apparent at the end of an hour or two; it continued at a decreasing rate for two to four days, and then it came to an end. We have kept many tubes for as long as a month, and some for as long as two years; but we have failed to find any noteworthy change after four days. In some tubes sealed at atmospheric pressure we have found that practically no change at all takes place, even during the first few hours.

It is surprising, if a difference of vapor pressure due to a difference in size exists in these systems (and the experiments show that it does, at least at first) that all the smaller droplets do not distil completely away to the larger, regardless of their position. The fact remains that they do not, nor have we ever been able to bring about such a result, in spite of the most scrupulous care in purifying the mercury and in cleaning the tubes. We believe that the main difficulty is due to a contamination or alteration of the surfaces of the droplets which progressively slows down and finally stops their distillation.

Many experiments were carried out as above, except that the tubes were fastened vertically in a thermostat at 25° C. when they were not being examined. The changes were not appreciably more regular, or different in rate, at constant temperature.

It was found in some experiments that when a tube with mercury droplets deposited throughout the length of its walls is fastened vertically in a thermostat at constant temperature there is a tendency for the mercury to distil from above downward. This is, of course, due to the fact that in such a system the pressure of the vapor falls off with increasing height. Attempts were made to study the rate of distillation of the droplets as a function of their distance above the bottom of the tube. We found that the changes which the droplets underwent were so irregular that no correlation of rate of distillation with height was possible. We attribute these irregulatities to contaminations of, or change in, the droplet surfaces.

This distillation due to difference in height interferes with the distillation from small droplets to large when the tubes are kept stationary, as in all the experiments hitherto described. Accordingly, we fastened our tubes upon the arms of a rotator which revolved in a vertical plane in the thermostat. This device served also to eliminate any temperature differences which might exist between different parts of the tube. Further experiments in highly evacuated tubes with this modification showed more regularity in the outline of the cleared spaces around the largest droplets, perhaps, but there was no other new feature.

We measured the changes which certain droplets suffered in given times in the hope of discovering some law governing this change. Five series of microphotographs of as many systems, taken at intervals of 12 hours, were prepared; and the images of four selected droplets, as close to the large

droplet of each system as possible were measured with a filar micrometer on each of four negatives from each series. It was found that the changes in diameter with time were very irregular. In the twenty series there was no recognizable uniformity of behavior, even in a general way. The centers of distillation and of condensation in such systems as these are so numerous that analysis of their mutual effects presents hopeless difficulties.

It was evident that simpler systems must be prepared if any regularity was to be discovered. After some trials the following method of getting such simpler systems was worked out. A fairly large droplet of mercury was introduced into a clean dry tube which had been provided at its closed end with a small bulb which could be sealed off later. After evacuating to 0.001 millimeter or less, and sealing and cooling the tube, it was held in one hand and struck sharply against the palm of the other. The mercury was thus broken up and its particles were projected to different parts of the tube, where they adhered to its walls. In many cases systems were formed in which several small droplets were very close to a large one. In case of failure, the excess mercury was used to sweep up all the droplets and the operation was repeated.

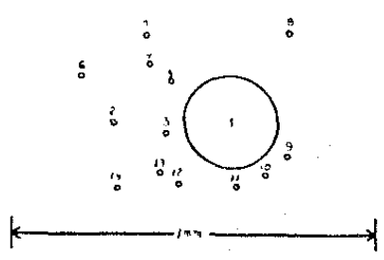


FIG. 7
Sketch of droplet system.

When a satisfactory system had been prepared, all other droplets were swept up, and the waste mercury run into the bulb prepared for it, which was then sealed off and rejected. The system was sketched as seen under the microscope, and a number was assigned to each droplet. They were then carefully measured with a filar micrometer and the mean of several determinations of different diameters was recorded. The tubes were rotated in the thermostat at 25° C. between measurements, which were made at varying intervals.

The results in one of the best of the experiments performed are shown in Table II. Fig. 7 shows the sketch of the corresponding system. As will be seen, the changes were hardly outside the limits of accuracy of the measurements which were made. Such experiments are almost wholly inconclusive.

We have succeeded in getting a very few systems in which one or two droplets about ten microns in diameter lay within 0.1 millimeter of large droplets. Careful studies of them after the manner described above showed that the small droplets scarcely decreased at all in diameter in a time as long as 60 hours.

In view of the slowness of the distillation from small droplets to large with mercury, and of the irregularities of the process, due presumably to surface changes, we are forced to conclude that numerical data upon the relation of vapor pressure to particle size cannot be had from experiments with them.

We were at first, completely at a loss to explain just why small droplets of liquids which wet glass do not distil over to larger ones, while the phenomenon is found with mercury, which does not wet glass, or wets it in less degree. A part of the explanation, it seems, may lie in the fact that droplets of wetting

liquids are very much flattened, and so do not have great curvature even when very small. We believe, however, that the real explanation lies in the nature of the deposits. If droplets of a liquid upon a surface which it wets are in equilibrium with a film of the liquid which is spread upon the surface between them, it follows from the definition of equilibrium that they have the same vapor pressure as does the liquid in the film, and so the vapor pressure of all the droplets is the same. It is not to be expected, then, that there will be any distillation from certain droplets to others unless some such influence as a difference in temperature brings it about.

TABLE II

The rate of distillation of small mercury droplets to large.
Diameters in millimeters at elapsed time:

Time in hours	0	26	55
Droplet 1	0.253	0.254	0.254
2	0.014	0.018	0.016
3	0.010	0.010	0.007
4	0.010	0.010	0.009
5	0.017	0.017	0.020
6	0.015	0.015	0.018
7	0.011	0.013	0.013
8	0.013	0.013	0.009
9	0.012	0.011	0.007
10	0.014	0.013	0.010
11	0.012	0.012	0.007
12	0.010	0.006	0.005
13	0.013	0.012	0.011
14	0.012	0.006	0.005

Crystals of Iodine and other Substances

No experiments have been more widely quoted in support of the Thomson equation than those having to do with the growth of large crystals at the expense of small ones by sublimation. We, too, have found instances of the growth of certain crystals at the expense of others by sublimation; but always under such circumstances that we were led to believe that differences of temperature were the most important, if not the only active cause. It seemed from our other work that, at constant temperature, sublimation should occur only very slowly and over very small distances between crystals of different sizes.

When iodine is heated rapidly in a closed system it may be made to melt *in situ*, and when it solidifies again the crystals which form adhere well to the surface on which they rest. Rather irregular crystal masses may be formed in this way. When the iodine which has been driven to other parts of the tube is now gently sublimed to the neighborhood of the larger crystals, this area being cooled by applying a wet cloth, systems consisting of large crystals closely surrounded by small ones are formed.

Three such systems were prepared in tubes which had been evacuated to a pressure of about one millimeter. It was found that the large crystals were 1 to 3.5 millimeters, while the smaller ones were close to 0.1 millimeter in greatest dimension. We have not succeeded in getting smaller crystals than this by sublimation. These tubes were rotated in the thermostat at 25° C. for a month, and removed and examined under the microscope at intervals. The small crystals were not cleared away from around the large ones, nor did they decrease appreciably in size during this time.

Experiments were carried out with very similar systems of iodine crystals in the "test tube" thermostat at the boiling point of chloroform, examining the crystals from time to time with a low power microscope without removing them from the bath. In these experiments, which lasted from eight to nine days, there was no clearing of spaces around the large crystals. No decrease in the size of the small crystals was detected.

Similar experiments with naphthalene and camphor were unsuccessful in that no distillation from small particles to large was found.

These experiments show that the difference in vapor pressure which is due to a difference in particle size must be negligibly small for crystals, unless some of them are very small indeed. For crystals of macroscopic size it must be practically non-existent. Yet these systems, which failed to show any change in constant temperature, never failed to show sublimation from one part of the tube to another when left for a few hours in contact with the air of the room, with its slight temperature differences.

Small and Large Meniscus

Another method by which it seemed that quantitative data might possibly be secured upon the relation between vapor pressure and particle size, or size of meniscus, was suggested by an experiment of Washburn.[1] He suspended a small capsule partially filled with water over water in a large vessel; and found that, at constant temperature, water distilled from the capsule down to the large sufrace. When he suspended the capsule with its liquid well below the level of the large surface, he found that water distilled from the large surface to the water in the capsule. Obviously, if the meniscus of water in the capsule had been brought to the proper level, so that the vapor pressure at its surface was equal to that at the large surface less the pressure of the column of vapor between these two levels, no distillation at all would have taken place. The pressure of the vapor in a system at any point above or below a plane surface may be calculated by means of a well known equation.[2] If, then, we can determine experimentally the height at which a small meniscus must be above a large surface to be in equilibrium with its adjacent vapor and neither gain nor lose liquid, we can calculate the vapor pressure. The practical applicability of the method will be determined by the rate at which distillation takes place to or from the small meniscus when near its equilibrium position.

[1] E. W. Washburn: J. Am. Ceramic Soc., **1**, 25 (1918).
[2] J. W. Mellor: "Higher Mathematics for Students of Chemistry and Physics," 61 (1922).

We prepared an apparatus in the form of an inverted U tube with large and small arms, as shown in Fig. 8. The arms had radii, respectively, of about 8 and about 1.5 millimeters. After cleaning and drying, the apparatus was filled nearly full of liquid. It was then evacuated, the liquid was boiled gently to ensure the expulsion of all air, and then it was sealed. The meniscus was brought to the desired position in the smaller tube, (the disposition of the meniscus in each tube was much as shown in the figure in every case), and the apparatus was completely immersed in the thermostat bath. After about two hours had been allowed for the liquid to drain from the walls, measurements were started. Thereafter the position of the small meniscus was determined from time to time with reference to a mark on the small tube, using a cathetometer with micrometer slide attachment which read to 0.001 millimeter.



FIG. 8

In experiments at 20° C. toluene and benzene showed no change in twelve hours. Water showed a very slight rise. Ether showed a rise of about 0.012 millimeters in that time. At 40° the rates for ether and water were somewhat more than doubled. At 50° the rates for both liquids were again somewhat more than doubled. Ether showed a rise of about 0.06 millimeters per hour at this temperature. These rates are very low, in spite of the fact that the surfaces were disposed so as to favor the distillation. With smaller capillary tubes we found the effect to diminish progressively, until tubes of radius about 0.4 millimeters were reached. These smallest tubes showed no effect at all, even with ether, during a period of several days.

This experiment was first proposed in a somewhat different form in Sir William Thomson's original article. It was actually tried by Bacon[1], who found that, in one year, less than 0.056 grams of ether has been transferred into a capillary tube in which ether orginally stood at about the same relative distance below the large surface as in our experiments.

It is evident from these experiments that a meniscus, near its equilibrium position, would rise or fall at a rate much too slow for measurement. The actual determination of the equilibrium position for such a meniscus seems impossible.

We made other experiments with a drop of benzene about two millimeters in diameter suspended from a ring of platinum wire about one centimeter above a large surface of benzene. The containing vessel was thoroughly exhausted before sealing. We kept it immersed in the water of a thermostat at 25° C. and the droplet was observed from time to time through a low power microscope. No change in the droplet could be certainly detected short of 24 hours, and a week was required for it to disappear. A very much smaller droplet suspended from a fine platinum wire in a similar apparatus under the same conditions disappeared only after the expiration of three days. This confirmed

[1] A. A. Bacon: Phys. Rev., (1) 20, 1 (1905).

our belief that distillation due to a difference in height is very slow. We concluded that we could not get quantitative experimental confirmation of the Thomson equation by experiments of this type.

Summary and Conclusion

Theoretical considerations have been given which lead us to the belief that the limits within which the Thomson equation is actually applicable must be very narrow.

Ostwald's experiment with sulfur droplets, wherein clear zones appear surrounding larger particles, is one of the most generally cited illustrations of the application of the Thomson equation. But we have found that whenever clear zones appear the central particle is solid. If all droplets are kept liquid no measurable distillation occurs. We have demonstrated this with sulfur and phosphorus and other liquids which wet glass.

We have found evidence which supports the conclusion that a liquid upon a surface which it wets forms droplets, in equilibrium with a film of liquid on the solid between them; a system analogous to that formed by an oil film on water or mercury. We believe that small droplets of wetting liquids, on glass, do not distil to larger ones because they form such systems.

With mercury, which either does not wet glass or wets it less than the substances above named, we found that larger globules grow at the expense of smaller, as have other observers. This is qualitative evidence in favor of the equation; but we found it impossible to secure data which would serve for a quantitative test. This distillation stops after the lapse of a few days in a singular fashion, explainable perhaps as due to contamination, perhaps to orientation of molecules in the surfaces.

We were unable to detect growth of larger crystals at the expense of smaller ones with such substances as iodine, naphthalene and camphor.

We found distillation between a large and a small liquid meniscus to be so slow that it would be useless to attempt to determine experimentally the equilibrium position of any meniscus, with reference to a large surface of the same liquid.

Persistent efforts extending over several years have failed to yield any quantitative experimental data supporting the Thomson equation. We conclude that the causes and effects formulated by that equation are so small that they are usually obscured or obliterated by other causes and effects always simultaneously present. Therefore it is not justifiable to refer to it as an explanation of phenomena so generally as is now the custom.

We do not presume to question any step in the logical thermodynamic reasoning leading to the Thomson equation. Indeed it was our faith in the accuracy of that reasoning which led us to hope so long that we should ultimately be successful in obtaining experimental confirmation. But our experience leads us to question the usefulness of the equation, either in explanations or in predictions.

S-227

GERMANIUM. XXIV. THE DIHALIDES OF GERMANIUM, TIN AND LEAD[1]

BY F. M. BREWER[2]

Recent investigation of the dihalides of germanium renders it now possible to make a comparative study of the dihalides of germanium, tin and lead, elements in the fourth group of the Periodic Table. The dihalides of carbon and silicon are as yet unknown. Examination of the available data concerning the physical constants of these compounds discloses wide discrepancies in the results reported by varoius observers. The most trustworthy values[3] appear to be the following:

Melting Points

	Germanium	Tin	Lead
Dichloride	Probably low-melting solid	247°	501°
Dibromide	122°	232°	? 373° ? 488°
Di-iodide	Sublimes with decomposition above 240°	320°	402°

Boiling Points

	Germanium	Tin	Lead
Dichloride	Not known	606°	954°
Dibromide	Volatilizes with some decomp. ca. 125°	619°	920°
Di-iodide	——	720°	(861° – 954°)

These data show that, as regards thermal stability, the dihalides of germanium exhibit properties quite in conformity with the position of the element in this group. At elevated temperatures they dissociate much more readily than do the dihalides of tin and lead, the decomposition proceeding

$$2\ GeX_2 = Ge + GeX_4$$

It is probable that the first stage in this dissociation is

$$GeX_2 = Ge + 2\ X$$

and that then the halogen acts upon the dihalide

$$GeX_2 + 2\ X = GeX_4$$

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[1] Contribution from the Department of Chemistry, Cornell University.

[2] This article is based upon part of the thesis presented to the Faculty of the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] A full list of references is given in Mellor's "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Volume VII.

In this connection the thermal behavior of the tetrahalides of these three elements and of the two elements at the head of the group, carbon and silicon, is of interest. Carbon tetra-iodide begins to decompose at 50°. The tetra-bromide dissociates somewhat when heated to boiling under atmospheric pressure. Carbon tetrachloride is a very stable substance which, when heated alone, breaks down only at elevated temperatures. The products in this case are mainly tetrachlorethylene and hexachlorethane, which indicates a primary decomposition

$$CCl_4 = CCl_2 + Cl_2$$

followed either by polymerization or by further dissociation of the dihalides according to the equations given above.

Much less is known of the behavior of the halides of silicon at elevated temperatures. There is, however, no reason to expect any fundamental difference from the behavior which the corresponding compounds of carbon should be expected to exhibit except that, as is seen in other groups of the Periodic Table, the compounds of silicon would probably be more stable and less reactive.

Coming to the tetrahalides of germanium, more data are available. Germanium tetrachloride does not dissociate[1] when heated to 950°. The thermal stability of germanium tetrabromide has not been directly studied but no dissociation was observed when the compound was distilled. (B. Pt. 185.9°)[2]. Germanium tetra-iodide, however, dissociates at 440° into germanium di-iodide and iodine.[3] All of the tetrahalides of tin are stable at their boiling points, but their behavior at higher temperatures has not been studied. It is, however, of interest to note that stannic iodide when dissolved in arsenic tribromide appears to dissociate[4] as follows:

$$SnI_4 = SnI_2 + 2\ I.$$

Lead tetrachloride decomposes explosively[5] into lead dichloride and chlorine at 105°.

It is thus seen that the dihalides of germanium, tin and lead show increasing thermal stability and decreasing reactivity with rise of atomic number of either the halogen or the group element. The tetrahalides, on the other hand, show decreasing stability with rise of atomic number.

When the dihalides of carbon and silicon are isolated, they will undoubtedly be found to be highly reactive. Even the polymerized form of carbon dichloride, tetrachlorethylene, readily takes up additional chlorine, and it may safely be predicted that the unpolymerized form would show greatly enhanced reactivity. This belief is supported by the observation in this Laboratory that germanium dichloride unites with chlorine with almost uncontrollable speed. The gradual lessening of the activity of the dihalides with rise

[1] Laubengayer and Tabern, J. Phys. Chem. **30**, 1047 (1926).
[2] Dennis and Hance, J. Am. Chem. Soc. **44**, 299 (1922).
[3] Dennis and Hance, J. Am. Chem. Soc. **44**, 2854 (1922).
[4] Walden: Z. anorg. Chem., **29**, 379 (1902).
[5] Friedrich: Ber., **26**, 1434 (1893).

of atomic number of the group element is shown by the fact that stannous chloride readily but quietly unites with chlorine in the cold, whereas lead dichloride takes up two additional atoms of chlorine only under special conditions, the resulting tetrachloride being quite unstable.

Behavior toward Oxygen (Reducing Power):—Here again the reactivity of the dihalide is less as the atomic number of the group element rises. Lead chloride, for example, is stable in the air and is only slowly decomposed when heated. Stannous chloride is fairly stable in air, and yields stannic chloride and an oxychloride when heated to its boiling point. Germanium dichloride is rapidly attacked by oxygen at room temperature. The dibromide and di-iodide are less readily affected by oxygen, the latter being converted to germanium dioxide and germanium tetra-iodide when heated in air to 210°.

As a direct corollary of the behavior toward oxygen, the reducing power decreases with rise of atomic number of the group-element, a solution of germanous chloride having powerful reducing action, whereas lead dichloride shows this property almost not at all.

Solubility Relationships and Hydrolysis:—The dihalides of germanium are but slightly soluble in hydrocarbons, but they react with liquids which contain an actual or a potential hydroxyl group. This action is presumably of hydrolytic nature, yet whereas the action of a small quantity of water on germanium dibromide is to produce a voluminous solid precipitate which may be either white or pale yellow in color, and which is soluble in excess acid, there is no such precipitate formed with absolute alcohol. The di-iodide reacts slowly with cold water, but is soluble in an excess. On the other hand, alcohol dissolves it readily, but the entire lack of color in the alcoholic solution indicates that possibly dissociation, but more probably alcoholysis, has taken place. Since recrystallization cannot be effected from either the colorless solution in water or that in alcohol, these solutions cannot be regarded as strictly analogous to the colorless solution of lead iodide in hot water.

Stannous halides are soluble in water. There is evidence of hydrolysis, but the salts can be recrystallized from aqueous solution in a hydrated condition. In contrast to this, the lead salts are remarkable for their extremely low solubility in cold water, and their inordinately steep solubility curves, hydrolysis being negligible.

With regard to non-polar solvents, stannous chloride is soluble to a small extent in benzene and some other non-hydroxylic solvents which are quite without action upon lead salts.

Solubility relationships may therefore be said to bear out the more definitely polar character of the di-iodide. That is to say, the di-iodide forms the link with the metallic or salt-like halides, whereas the dichloride and dibromide are more closely allied to the halides of the non-metals and metalloids. As might be expected from certain theories of solution involving similarity of constitution between solvent and solute, the most effective solvents for germanous chloride and bromide appear to be the corresponding tetrahalides.

The solution of the colorless dibromide in germanium tetrabromide is yellow in color, and it is possible that the colorless solid is a polymer, while the yellow solutions contains the unassociated $GeBr_2$. This polymerization is seen in the case of stannous chloride which near its boiling point has a vapor density that indicates the presence of molecules of the polymer Sn_2Cl_4.

The Significance of the Chloroform Series.—Of still greater significance are the chloroforms of the five elements. The reactions between the known dihalides of the fourth group and the corresponding hydrogen halides present a most fascinating, as well as a most comprehensive, picture of the valency relationships in the group.

Chloroform is essentially a non-polar compound. It is extremely volatile, is soluble in non-dissociating solvents, and gives a non-conducting solution in dissociating solvents. Bromoform is similar in all respects. Iodoform is rather less stable, decomposing when heated above its melting point. Its color suggests the possibility of an internal complexity not revealed by the other two compounds. Even so, there is no suggestion of electrolytic dissociation, or that iodoform is anything but a neutral organic compound. The physical constants of the silicon compounds are parallel to those of the corresponding carbon derivatives.

On the other hand, the chemical characteristics of these compounds implies a greater differentiation between the atoms attached to the carbon or silicon than would be expected from simple derivatives of methane. It is only necessary to consider chloroform itself. Dumas first pointed out the relation of chloroform to formic acid, which, in its reducing power, and in its intimate connection with carbon monoxide, is in direct contrast to the saturated hydrocarbons. Since alkali converts chloroform into alkali formate, it is to be expected that alkaline oxidizing agents will be reduced by chloroform. But chloroform reduces potassium permanganate and potassium dichromate in acid solution almost as well. The oxidation products are phosgene and chlorine, which are essentially the oxidation products of carbon dichloride and hydrogen chloride respectively. These two compounds are probably the primary products of the thermal dissociation of chloroform vapor. Even more startling is the action of a concentrated solution of silver nitrate upon iodoform, which results in the cold in the formation of silver iodide and carbon monoxide. The latter may be regarded as a direct hydrolytic product of carbon di-iodide. Instances might in fact be multiplied to show that compounds of this type react in the majority of cases as if they underwent a primary dissociation into a dihalide and hydrogen halide.

As regards the analogous compounds of germanium, there is no question that this dissociation is the dominating characteristic of compounds of the chloroform type. The formation of germanium chloroform from germanium dichloride and hydrogen chloride does not appear to be reversible, but the hydrolysis of the product yields a solution possessing all the properties associated with germanous compounds. It is a powerful reducing agent, and yields the monosulphide, and the brown, hydrated monoxide with appropriate reagents.

In the case of germanium bromoform, thermal dissociation begins in the neighborhood of 10°, and it has not been found possible to preserve the germanium analogue of iodoform above 0° except in the presence of hydrogen iodide. This compound is all the more interesting since it again forms the true connecting link between the metallic and the non-metallic elements of the group.

Since it has been discovered that tin and lead form volatile hydrides, there is no *a priori* reason why their partially substituted halogen derivatives should not preserve a non-polar continuity in physical properties, similar for instance to that which occurs with the tetra-chlorides. An examination of the available data shows, however, that this is not the case. The hypothetical addition product of hydrogen chloride and stannous chloride is not regarded as a non-polar body, but rather as the parent acid of the chlorostannites, which are perfectly definite complex salts. By crystallizing stannous chloride from concentrated hydrochloric acid hydrates of the complex acid are said to be formed. The existence of $SnI_2 . HI$ as a solid phase has been demonstrated by indirect analysis, although the compound itself was found to be unstable. Finally, in the case of lead salts, the only connection is to be found in the solubility relationships. The solubilities of the halides of lead are at first decreased by the addition of the halogen hydracid to their solutions, owing to the common ion effect, but are eventually increased with increased concentration of acid owing to the formation of more soluble complexes.

With the extensive range of variation that this series affords, yet marked nevertheless by such regular gradation, there can be little doubt that in the nature and behavior of the germanium compounds lies a very important key to a generalized theory of chemical combination. No attempt will be made to develop any such theory here, but there is one question involving general principles which may well be discussed at this point. The tetravalency of carbon in chloroform has long been tacitly accepted, and by analogy one would expect germanium chloroform to behave as though it contained tetravalent germanium. Actually it is much more intimately related to the dichloride than to the tetrachloride, and the problem consequently arises as to the true valency of germanium in this compound.

Valency is an electronic function, and there are only two main possibilities. Electrons may be transferred completely from one atom or group of atoms to another, combination being effected by simple electrostatic attraction between the charged systems so formed. This constitutes combination by polar or electro-valency. In the case of non-polar valency, electrons may be influenced simultaneously by two or even more nuclei, in which case it is impossible to dissociate one nucleus from the other without altering the properties of both. An ion, on the other hand, can act as an independent entity. It is therefore clear that the criterion which enables the distinction to be made between these two types of combination is that of electrolytic dissociation. Nevertheless it cannot always be said that a substance is *per se* an electrolyte, for ionic dissociation is determined by circumstantial conditions, and a compound

which is dissociated in water may give a non-conducting solution in a non-polar solvent.

It will be obvious that non-polar valency must include all those phenomena designated previously by such terms as co-valency, residual valency, or molecular combination, and though the actual mechanics of non-polar valency is not yet understood, there cannot very well be any sharp differentiation between one kind of attachment and another in this general class. There must indeed be possible continuous variation in the strength of such attachments until the minimum limiting value is reached at which ionic dissociation will occur.

Regarded in this light, the question of the constitution of germanium chloroform is considerably simplified. It is not essential to decide between a formula $GeCl_3H$ (a derivative of tetravalent germanium) and the molecular compound $GeCl_2 . HCl$. The hydrogen and the chlorine must be held by some attractive force, whether it is called residual valency or by any other name, and it is highly improbable that the two chlorine atoms should be responsible for this attachment with unsaturated germanium present. In other words, all four atoms are probably attached to the germanium by non-polar bonds. To explain the reactions of the compound it will then be necessary to show why two of the bonds are so very weak; and not only why they are weaker than the other two, but why they are weaker than the corresponding bonds in the chloroforms of carbon and silicon, and finally why this differentiation is not shown to any extent in the tetrachlorides of all three elements.

The answer depends upon two principles, one of which is reasonably obvious and generally accepted. It is that in any group of the Periodic Table—and for this purpose the subgroups must be regarded as independent of each other—the tendency to form positive ions increases with increasing atomic number. The tendency to form non-polar compounds will simultaneously decrease. The second principle is less obvious and its effect is of a secondary nature. It appears therefore only in the comparison of those compounds which are sufficiently similar to render other influences approximately constant. Briefly, it may be stated as follows:—that, other things being equal, there is an intimate correlation between symmetry and stability. Isolated cases have long been recognized. The stability of the inert gases is ascribed to the symmetry of their electronic constitution. The stability of such structures as the paraffins of the benzene ring are fundamental axioms of organic chemistry and the disturbing influence of single substituents in otherwise comparatively inert molecules is well-known. But the principle is worthy of even wider application, and a noteworthy instance is seen in the case of germanium chloroform.

In the first place, it explains why the reactions of the chloroform are essentially those of the dichloride plus hydrogen chloride. Every reaction which has been studied so far has permitted the substitution for the hydrogen and one atom of chlorine either of two similar atoms or groups of atoms, or else of one doubly-bonded and therefore symmetrically placed single group. Either of these arrangements is more symmetrical than the original one, and

therefore the chloroform tends to lose hydrogen chloride so that they can be established. It thus reacts as if it were dichloride. If this were not the case the bromination of germanium chloroform should yield hydrogen bromide according to the equation

$$2\ Br + GeCl_3H = GeCl_3Br + HBr$$

But it was observed in this Laboratory that the evolved gas was hydrogen chloride, and that the resulting germanium compound contains both chlorine and bromine. The only symmetrical product which could here be formed is $GeCl_2Br_2$. The fact that hydrogen chloride is more stable than hydrogen bromide no doubt assists.

The relative stability of the chloroforms of carbon, silicon, and germanium is fully explained by the first principle involved, namely, that of increasing tendency to form the ionized, rather than the tetravalent or non-polar type of compound, but the value of the second principle is again manifest when it is recalled that the series of tetrachlorides is maintained from carbon to lead, as is the series of the tetrahydrides. Yet the chloroform series ceases to exist, at least as a non-polar series, with the element germanium. But for any given element, the tetrachloride and the tetrahydride, being symmetrical, should be more stable than the unsymmetrical chloroform.

It is of interest to note that chloroform is reduced by zinc in alcoholic solution to the more symmetrical dichlormethane. The isolation and investigation of the silicon and germanium analogues of this compound, though undoubtedly difficult, would afford an excellent test of the validity of the theory.

Ithaca, New York.

THE PHYSICAL CHEMISTRY OF COLOR LAKE FORMATION. III. ALIZARIN LAKES

BY HARRY B. WEISER AND EVERETT E. PORTER

Alizarin or dihydroxy anthraquinone is the most important mordant dye. It was formerly obtained from the roots of madder, a plant of Indian origin, which was cultivated largely in France and in Holland before its synthesis from anthracene was accomplished in 1868. The chief mordants for the dye are alumina which yields a red lake, chrome which yields a reddish brown, tin which gives an orange, and iron which gives purple or black. If the fiber is treated with the so-called sulfonated oils before mordanting with alumina, there results the brilliant Turkey-red, a color remarkable for its fastness to light and to the action of soap and water.

Since, in general, alizarin is not taken up by alumina in the absence of calcium, the lake is usually assumed to be a calcium aluminum alizarate.[1] It is claimed that strontium, barium, and magnesium may be substituted for calcium but the former are not satisfactory. Davison[2] found that hydrous alumina prepared from aluminum acetate takes up more alizarin in the absence of calcium salts than that prepared from the sulfate. Since the alumina mordant bath is aluminum sulfate, Bancroft[3] concludes that the function of the calcium is not to fix the alumina on the fiber or the dye to the mordant but to remove sulfate which cuts down the adsorption of alizarin. If this were true, soluble barium salt would be more satisfactory than calcium salt. As we shall see, the function of calcium ion is to increase the adsorption of alizarin ion and not to cut down the concentration of sulfate.

Biltz[4] was the first to suggest that the alizarin lakes might not be definite chemical compounds. Thus with hydrous chromic oxide the amount of alizarin SW taken up increases continuously with increasing concentration of solution showing no indication whatsoever of the formation of chromium alizarate. On the other hand, with hydrous ferric oxide there was a rather marked increase in the amount of alizarin taken up with relatively small change in the equilibrium concentration, leading Biltz to conclude that iron and alizarin combine in the ratio of one molecule of Fe_2O_3 to three molecules of alizarin. But the amount of alizarin taken up by the iron oxide is far in excess of that necessary to form alizarate, hence one is confronted by the necessity of assuming either that alizarate adsorbs the excess of dye or that the whole phenomenon is a case of adsorption of the dye by the oxide. Recently the iron and aluminum lakes of alizarin have been investigated in

[1] J. Soc. Chem. Ind., **5**, 525 (1886).
[2] J. Phys. Chem., **17**, 737 (1913).
[3] J. Phys. Chem., **18**, 1 (1914).
[4] Ber., **38**, 4143 (1905).

Bancroft's laboratory[1] and the conclusion reached that the lakes are adsorption complexes of sodium alizarate and the hydrous oxides of the iron and aluminum respectively. Since this conclusion could not be reconciled with our observations on the taking up of dyes by the hydrous oxides, a systematic investigation of the alizarin lakes and the factors influencing their formation was undertaken.

Experimental Procedure

As in earlier experiments the metallic mordants, ferric oxide, chrome, and alumina were prepared as sols. These were precipitated by the addition of the alizarin dye, sodium alizarate or alizarin SW, at varying hydrogen ion concentrations and the adsorption determined from the change in the concentration of the supernatant solution. The hydrogen ion concentration was varied by the addition of varying amounts of either sodium or potassium hydroxide or hydrochloric acid. Since alizarin is not affected by the hydrogen electrode under the conditions of the experiments, the initial and final pH values were determined accurately.

Analysis of Alizarin. The accurate determination of alizarin and its simple derivatives called for a special investigation, since Knecht's method of titration with titanous chloride was found to be unsatisfactory. The procedure adopted consists in getting favorable conditions for the oxidation by permanganate of alizarin to phthalic acid without the precipitation of any manganese dioxide. In working out the experimental details, the quantity of dye was varied between 0.01 and 0.001 millimoles, this being the approximate range of quantities to be analyzed in the adsorption experiments. The following procedure was found to be satisfactory: To the solution containing the alizarin in about 25 cc is added 5 cc of concentrated sulfuric acid and 2 cc of M/2 manganous sulfate. To this solution, boiling hot, is added N/50 potassium permanganate avoiding an excess of more than one cubic centimeter at any stage of the titration. The addition of the potassium permanganate, a little at a time, is continued until there appears to be no further reduction after boiling for from 20 to 30 seconds in the presence of an excess of from one half to one cubic centimeter. A little practice enables one to tell from the color of the solution when the proper excess of reagent has been added. If the excess is much more than 1 cc, manganese dioxide is precipitated and if too small the oxidation is incomplete. After the oxidation is complete, the solution is cooled to about 70° and a small excess of oxalate added. Potassium permanganate is again run in to the usual end-point. Some representative data on the accuracy of the method for the concentrations used in this work are given in Table I. The suitability of the method was not tested for large quantities of dye. The theoretical equivalent/molar ratio is 26, provided the reaction goes quantitatively to phthalic acid, carbon dioxide, and water. The observed ratios are low but consistently so. No other method was found which compares at all favorably with this one for the determination of such small quantities of the alizarins.

[1] Bull and Adams: J. Phys. Chem., **25**, 660 (1921); Williamson: **28**, 891 (1924).

TABLE I

Titration of Alizarin with Potassium Permanganate

Cc 0.0006 M soln. alizarate titrated	Cc N/50 $KMnO_4$ required	$\frac{\text{normal}}{\text{molal}}$ ratio
20	13.09	23.5
20	13.09	23.5
20	13.07	23.4
5	3.02	20.2
5	3.27	21.8
5	3.08	20.3
2	1.30	23.4

The Adsorption of Alizarin SW

The sodium salt of alizarin mono-sulfonate was chosen for the initial experiments for several reasons: It is easy to determine quantitatively even in small amounts; it is not reduced at the hydrogen electrode in dilute solution; its acid is sufficiently soluble that no precipitation takes place throughout a wide pH range; and finally, it is readily purified and weighed.

Adsorption by Hydrous Chromic Oxide. The data for the adsorption of alizarin SW by hydrous chromic oxide at varying hydrogen ion concentrations is shown in Table II and represented graphically in Fig. 1. The pH curve for the acid and alkali alone in the same total quantity of water is also given. The length of a horizontal line drawn from any point on the curve for the pH

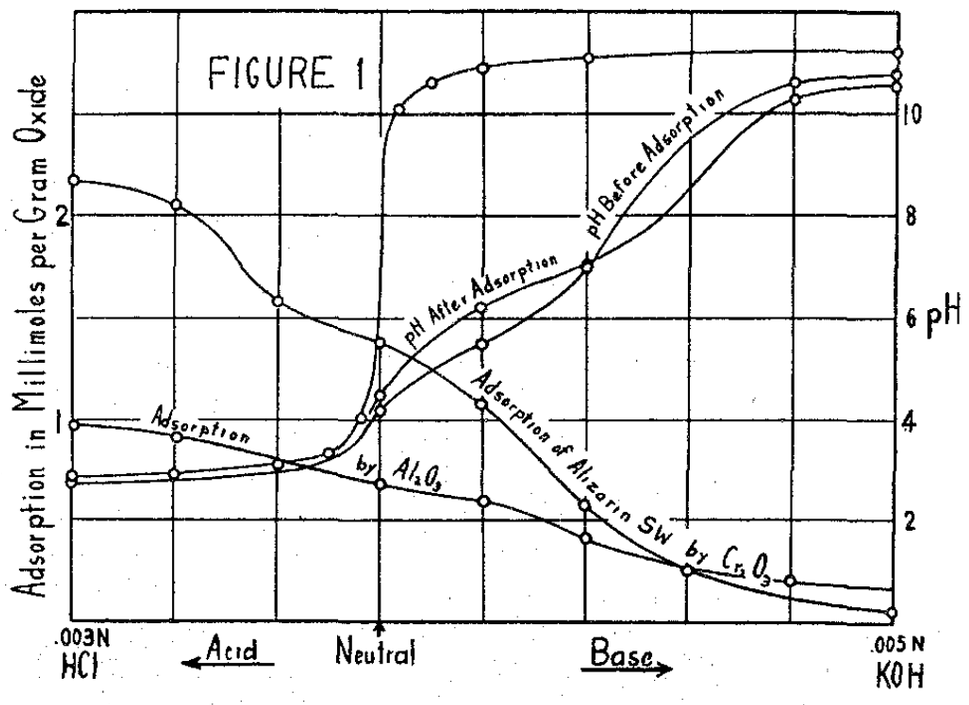
TABLE II

Adsorption of Alizarin SW by Hydrous Chromic Oxide at varying pH Values

Cc of soln. mixed with 5 cc of sol containing 0.0125 gram of Cr_2O_3 in a total of 20 cc			Adsorption value in millimoles alizarin SW per gram Cr_2O_3	pH values		
0.04 N HCl	0.037 N KOH	0.01 M dye		without dye or colloid	without colloid	total mixture
2.5	0	5	2.46	2.86		2.419
1.5	0	5	2.40		2.400	2.717
1.0	0	5	2.32		2.727	2.822
0.5	0	5	2.18	3.11	2.873	3.042
0	0	5	1.70		4.173	4.478
0	0.57	5	1.41	10.62	5.490	6.170
0	1.13	5	1.15		7.554	7.556
0	2.27	5	0.16		10.529	9.283
0	3.39	5	0.09	11.17	10.634	10.445

of the mixture without the colloid to the acid-alkali curve, gives the quantity of acid or base reacting with the dye. The curve is continuous giving no indication of the formation of a compound at any pH value. As would be expected, there is quite a buffer effect in the titration of the mono-sodium to the di-sodium salt. Moreover, there is a corresponding holding up of the

adsorption-concentration curve in this region. This has two causes: the concentration of the hydroxyl ions is not increasing in proportion to the alkali added; and, at the same time, the concentration of the highly adsorbable dye ions is rapidly increasing. Just as was found in the case of sulfate and of oxalate,[1] hydroxyl ion may completely displace the dye, the latter requiring a slightly higher hydroxyl ion concentration than the former. This indicates that the dye is more strongly adsorbed than either sulfate or oxalate but is not so strongly adsorbed as hydroxyl.



Adsorption by Hydrous Alumina. The observations on the adsorption of alizarin SW by hydrous alumina are given in Table III and plotted in Fig. 1. Since the adsorption capacity of the alumina is much less than that of chromic oxide, a larger sample of the former was used in the adsorption studies. The graphs show the same general effects of the hydrogen ion concentration as was pointed out in the case of the chromic oxide, the difference being that the effects are less pronounced with alumina than with chromic oxide in both the acid and basic baths. Here also, there is no indication of compound formation between the dye and the mordant at any hydrogen ion concentration investigated.

It was found impossible to study the adsorption of alizarin SW by hydrous ferric oxide through a wide range of pH values, since the pH value zone in which the precipitation of the sol is complete, is very narrow in the presence of a constant amount of dye, and the accurate determination of the hydrogen ion concentration is impossible when the removal of the iron is incomplete. As would be expected, the zone of complete precipitation shifts toward the acid range with increasing concentration of dye due to the strong adsorption of

[1] J. Phys. Chem. **31**, 0000 (1927).

TABLE III

Adsorption of Alizarin SW by Hydrous Aluminum Oxide at varying pH Values

Cc of soln. mixed with 5 cc of sol containing 0.0179 gram of Al_2O_3 in a total of 20 cc			Adsorption value in milliomoles alizarin SW per gram Al_2O_3	pH values		
0.04 N HCl	0.037 N KOH	0.01 M dye		without dye or colloid	without colloid	total mixture
2.5	0	0		2.86		
2.0	0	5			2.400	
1.5	0	5	0.98			2.345
1.0	0	5	0.90		2.722	2.799
0.5	0	5	0.86	3.11	2.873	3.363
0	0	5	0.66		4.173	5.097
0	0.57	5	0.61	10.62	5.490	6.384
0	1.13	5	0.41		7.554	7.915
0	2.27	5	0.26		10.529	9.931
0	3.39	5	0.22	11.17	10.634	10.896

the dye anion. The ease of reversibility of the ferric oxide sol will come up again in some observations to be reported in a later section.

Adsorption of Alizarin

Since the anion of alizarin SW is adsorbed by basic mordants giving color lakes whose composition is indefinite, depending on the concentration and pH value of the dye bath, there seemed to be no reason for believing that alizarin would react with ferric oxide to give ferric alizarate as Biltz believed. Bull and Adams[1] shook up a solution of sodium alizarate with ferric oxide and concluded that ferric alizarate was not formed since the hydroxide equivalent to the alizarate was not set free as would happen if a double decomposition reaction took place. The absence of any appreciable quantity of alkali in the bath led to the further conclusion that the lakes are adsorption complexes between ferric oxide and sodium alizarate. Similar conclusions were reached by Williamson[2] with reference to the alumina-alizarin lakes. It was difficult for us to see how this conclusion could be correct for all of our observations showed that when the hydrous oxides are brought in contact with highly ionized salts which yield a strongly adsorbed anion, it is the anion and not the molecule of the salt which is adsorbed. To settle this question the following experiments were carried out:

Pure sublimed alizarin was dissolved in the theoretical amount of sodium hydroxide to give sodium alizarate and the solution diluted to give a M/100 solution of the salt. Preliminary experiments were carried out to determine the maximum ratio of sodium alizarate to oxide which could be used and still have a nearly exhausted bath.

[1] J. Phys. Chem., **25**, 660 (1921).
[2] J. Phys. Chem., **28**, 891 (1924).

For the chromic oxide sol, 113 cc containing 1.42 grams of Cr_2O_3 was required to decolorize 100 cc of the sodium alizarate solution. The solutions were mixed in this proportion and 100 cc of the supernatant liquid was withdrawn and analyzed for sodium; for it was obvious that if the sodium alizarate were adsorbed as the salt, no sodium would remain in the bath. The sodium sulfate was found to be 0.0568 grams. On the basis of equal distribution throughout the mixture, there should have been found 0.0665 grams. Hence more than 85 percent of the sodium remained in the bath.

For the ferric oxide 237.5 cc of the sol was mixed with 50 cc of the M/100 sodium alizarate. After mixing the supernatant liquid was analyzed for sodium as in the previous case and 0.0253 grams of sodium sulfate was found as compared with 0.0284 grams if none were adsorbed. That is, about 90 percent of the sodium was left in the bath.

For the test on alumina lake, a gel was employed instead of a sol. A solution containing about 7 grams of aluminum chloride was precipitated by the gradual addition of ammonium hydroxide. This was washed by decantation with the aid of the centrifuge until peptization was just started. The matted gel occupied about 60 cc. The addition of one cc of the M/100 sodium alizarate caused nearly complete peptization of the gel. When 5 cc had been added the peptization was complete and the liquid was almost as fluid as water. Cataphoresis experiment on a similar sample showed it to be a negative sol. The addition of more of the sodium alizarate did not have any apparent effect until the total quantity present was 25 cc. The viscosity increased greatly from this concentration to a total of about 32 cc. More than this started precipitation and when 40 cc had been added, the precipitation was complete. The supernatant liquid was nearly colorless showing that the alizarin was practically all removed in the process. An aliquot part of the supernatant liquid, determined by weight, was analyzed for sodium. It was found to contain 0.0262 grams of sodium as sulfate compared with 0.0271 grams if none had been adsorbed. This shows that nearly 97 percent of the sodium was left in the bath. If the gel of ferric and chromic oxide had been used it is probable that the amount of sodium remaining in the bath would have been greater than when the highly purified sols were employed. It seems likely that the sodium which is taken up during the precipitation of the sols, is adsorbed as univalent alizarate ions containing one atom of sodium. The pH values of the colorless supernatant liquids showed them to be almost neutral.

It should be mentioned in passing, that the addition of sodium hydroxide to a washed gel of alumina gives results which are not unlike those with sodium alizarate. The gel is first peptized as a negative sol and on the addition of a critical amount of alkali it is reprecipitated giving a supernatant liquid which is nearly neutral and contains most of the sodium. This behavior is what might be expected since both the dye and the base are strongly adsorbed by the hydrous oxides.

The question naturally arises, how alizarate and hydroxyl ions could be adsorbed by a precipitated gel leaving practically all the sodium in the solu-

tion, without imparting a negative charge to the particles. For this to happen there must be adsorbed along with the hydroxyl and alizarate an equivalent quantity of some positive ion other than sodium or there must be liberated an equivalent quantity of some negative ion. The latter is what happens chiefly since it was found that the sodium is associated with chloride which was present in the gel and was replaced by the more strongly adsorbed hydroxyl or alizarate ions. This suggests that a gel from which practically all the chloride was removed would have a very small capacity for adsorbing anions.

To test this, hydrous chromic oxide was employed since it is the best adsorbent of the oxides of the iron group. The sol containing 1.42 grams of Cr_2O_3 was precipitated with ammonia and washed repeatedly with the aid of the centrifuge keeping the washing very slightly alkaline with ammonia. By this procedure practically all of the chlorine was removed. After washing the gel several times with pure water it was suspended in a little water to which 0.5 cc of the M/100 sodium alizarate solution was added. After shaking and centrifuging the supernatant liquid was found to be colored showing that there was little or no adsorption of the dye. On comparing this result with the experiment described above in which 100 cc of the same dye solution was exhausted by a like amount of the sol, one sees to what extent the adsorption is dependent on the nature and extent of purification of the gel. In the last instance the gel was washed with water containing ammonia; the adsorption capacity of the particles was practically saturated with hydroxyl ions, and therefore the gel could take up but little of the dye anion. In the first experiment, on the other hand, the conditions were exactly reversed. The sol was peptized by acid and even after prolonged dialysis, the particles were positively charged owing to the preferential adsorption of the hydrogen ion. The sol contains an equivalent amount of the less strongly adsorbed chloride ion, a part of which is adsorbed by the particles and the remainder is present in the intermicellar liquid. On adding sodium alizarate, the strongly adsorbed alizarate and hydroxyl ions not only neutralize the sol by adsorption but displace the adsorbed chloride ion more or less completely.

Simultaneous Adsorption of Alizarate and Other Ions

The addition of sulfate to the acid baths which give up their color too rapidly has long been followed by the practical dyer. The sulfate by decreasing the adsorption and by retarding the rate of adsorption of the dye anion, tends to give a more even dyeing of the fabric.[1] Sometimes, however the presence of even a small amount of sulfate is objectionable; this is particularly true in the case of the alizarins. As already noted, Bancroft assumes that the purpose of adding calcium ion as calcium acetate to an alizarin bath is not to give a calcium aluminum alizarate of some sort on the mordanted cloth but to remove sulfate ion which cuts down the adsorption of alizarin ion. As will be seen in the next section, calcium sulfate is too soluble to enable one to account for the action of calcium ion in this way.

[1] Bancroft: J. Phys. Chem., **18**, 1 (1914).

Pelet-Jolivet[1] has demonstrated that readily adsorbed anions such as sulfate and phosphate cut down the adsorption of acid dyes (e.g. crystal ponceau) and readily adsorbed cations such as magnesium increase the adsorption of acid dyes.[2] Davison[3] made some qualitative observations on the effect of sulfate ions and of calcium ions on the adsorption of dyes by fibers as well as by alumina. Thus he finds that 8 grams of Na_2SO_4 in 100 cc of bath prevents the dyeing of wool by Crocein Violet. In lower concentrations, the dye is taken up in increasing amounts as the concentration of the sulfate is decreased. Alumina precipitated from aluminum acetate was found to adsorb certain acid dyes, including alizarin, more strongly than that from aluminum sulfate. Calcium acetate was found to increase the adsorption of the acid dye Crocein Orange but to decrease the adsorption of the acid dye Acid Green. There are other inconsistencies such as one might expect in qualitative observations.

In the subsequent paragraphs are given the results of quantitative observations on the effect of both sulfate ion and of calcium ion on the adsorption of alizarins by mordants at varying hydrogen ion concentrations. The observations show clearly the action of neutral salts on color lake formation.

The Effect of Sulfate on the Adsorption of Alizarin SW. A series of observations was made to determine the effect of sulfate on the adsorption of alizarin SW by hydrous chromic oxide at varying pH values. The method of procedure was essentially the same as was used in determining the effect of sulfate on the adsorption of oxalate in an earlier paper.[4] The data are summarized in Table IV and plotted in Fig. 2. Just as in the case of oxalate it will be noted that the sulfate has little effect on the adsorption of alizarin SW anion in the neutral and basic solutions since, under these conditions, the presence of the much more strongly adsorbed hydroxyl ion masks the relatively small effect of the sulfate. In the acid range, however, the effect of sulfate is quite marked. Since the dye anion is adsorbed more strongly than sulfate from the same concentration, one might expect the latter to have little effect on the adsorption of the former. But the behavior of the dye is similar to that of the oxalate. In the acid solution the effective concentration of the dye becomes very small due to the suppressing of the ionization, and the action of sulfate manifests itself. If the sulfate had been determined in the series of experiments the results would have been similar throughout to those obtained with sulfate and oxalate; viz, sulfate adsorbed more from the acid and dye adsorbed more from the neutral and basic bath. Since acid baths are usually employed in dyeing acid dyes, the retarding effect of sulfate is explained even though the dye cation may be more strongly adsorbed than sulfate ion from the same concentration.

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[1] "Die Theorie des Färbeprozesses," 94, 98, 119, 148 (1910).
[2] Bancroft: J. Phys. Chem., **18**, 11 (1914).
[3] J. Phys. Chem., **17**, 737 (1913).
[4] J. Phys. Chem. **31**, 0000 (1927).

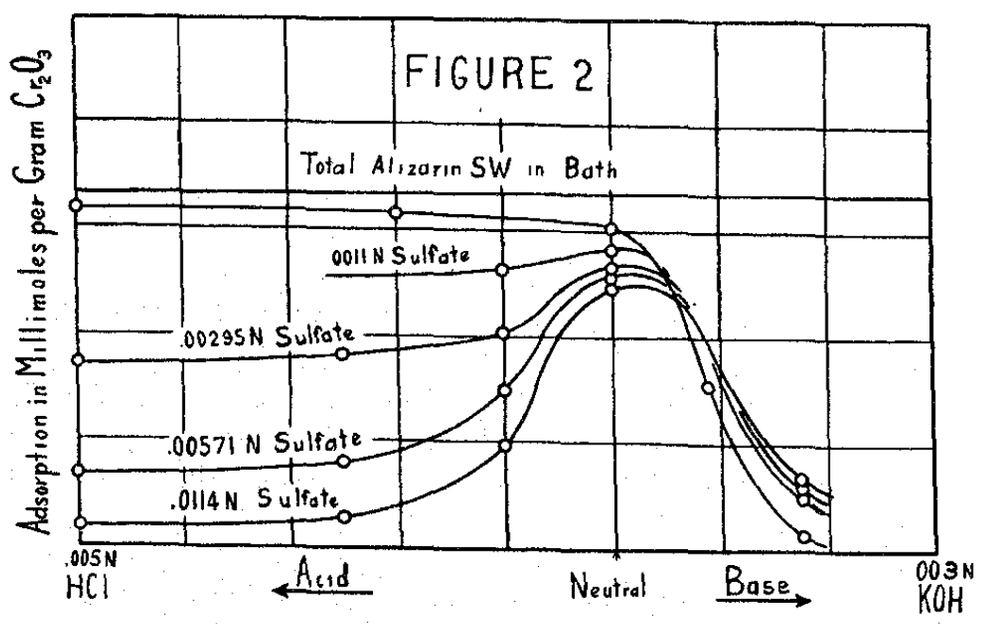


TABLE IV

Adsorption of Alizarin SW at varying pH Values in varying Concentrations of Sulfate Ion

Cc of soln. mixed with 10 cc of sol containing 0.0125 gram of Cr_2O_3 in a total of 35 cc.					Adsorption value in millimoles alizarin SW per gram Cr_2O_3	pH of mixture
0.04 N HCl	0.02 N H_2SO_4	0.02 N K_2SO_4	0.037 N KOH	0.003 M dye		
5	0	0	0	10	1.64	2.507
2	0	0	0	10	1.63	2.800
0	0	0	0	10	1.52	4.212
0	0	0	1	10	0.77	8.321
0	0	0	2	10	0.06	9.174
0	2	0	0	10	1.30	2.870
0	0	2	0	10	1.39	5.000
5	5	0	0	10	0.84	2.416
0	5	0	0	10	0.89	2.586
0	2	3	0	10	1.02	2.998
0	0	5	0	10	1.31	4.907
0	0	5	2	10	0.25	8.887
0	10	0	0	10	0.33	2.361
0	5	5	0	10	0.39	2.699
0	2	8	0	10	0.74	3.280
0	0	10	0	10	1.27	5.512
0	0	10	2	10	0.29	9.161
0	10	10	0	10	0.08	2.484
0	5	15	0	10	0.14	2.876
0	2	18	0	10	0.49	3.431
0	1	19	0	10	0.85	3.815
0	0	20	0	10	1.22	6.012
0	0	18	2	10	0.33	8.817

The Effect of Calcium Ion on the Adsorption of Alizarin SW. The results of the observations on the adsorption of alizarin SW in the presence of varying amounts of calcium ion as well as varying hydrogen ion concentrations are given in Table V and plotted in Fig. 3. Just as the effect of sulfate ion is

TABLE V

Adsorption of Alizarin SW at varying pH Values in varying Concentrations of Calcium Ion

Cc of soln. mixed with 5 cc of sol containing 0.0125 gram of Cr_2O_3 in a total of 35 cc.				Adsorption value in millimoles alizarin SW per gram Cr_2O_3	pH of mixture
0.04 N HCl	0.0137 N $CaCl_2$	0.037 N KOH	0.006 M dye		
2	0	0	5	1.62	2.606
1	0	0	5	1.58	3.000
0	0	0	5	1.52	4.212
0	0	1	5	0.77	8.321
0	0	2	5	0.06	9.174
2	2	0	5	1.62	3.103
0	2	0	5	1.54	4.904
0	2	1	5	1.46	8.206
0	2	2	5	0.83	8.924
0	2	4	5	0.20	10.311
2	4	0	5	1.63	3.010
0	4	0	5	1.57	4.490
0	4	1	5	1.59	5.892
0	4	2	5	1.35	9.044
0	4	4	5	0.30	10.379
1	6	0	5	1.63	3.100
0	6	0	5	1.58	4.239
0	6	1	5	1.62	8.512
0	6	2	5	1.61	8.683
0	6	4	5	0.91	10.031
1	10	0	5	1.63	3.091
0	10	0	5	1.61	4.247
0	10	1	5	1.65	8.152
0	10	2	5	1.63	8.248
0	10	4	5	1.63	9.049

small in the presence of the relatively highly adsorbed hydroxyl ion, so the effect of calcium is small in the presence of the relatively strongly adsorbed hydrogen ion. The effectiveness of the calcium increases with its concentration and with the concentration of the base until the solution becomes sufficiently basic to overbalance the calcium ion effect. From this one would expect the presence of a strongly adsorbed cation such as calcium to be particularly effective in the application of dyes that are insoluble in the acid bath. This

is the function of the calcium in dyeing with alizarin. Thus, in the presence of calcium one may use a slightly basic bath in which the alizarin is soluble and at the same time increase the adsorption of the dye anion so that it is not replaced by the hydroxyl.

All of the data of Tables IV and V were plotted adsorption against pH and the increase in adsorption due to calcium, as well as the decrease due to the sulfate read off at constant pH values. The resulting data are tabulated

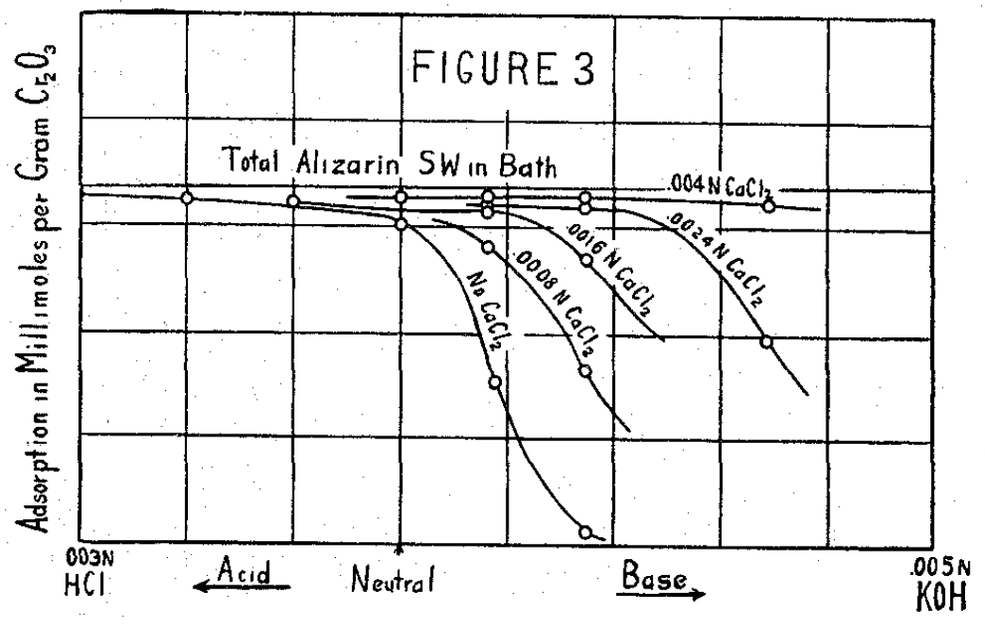


TABLE VI

The Effect of varying the Concentration of Salts on the Adsorption of Dye at Constant pH

The effect of calcium chloride			The effect of potassium sulfate		
N conc. $CaCl_2$	Increase in Adsorption at		N conc. K_2SO_4	Increase in Adsorption at	
	pH = 9	pH = 5		pH = 3	pH = 5
0.0008	0.50	0.05	0.0011	0.29	0.12
0.0016	1.17	0.065	0.0029	0.81	0.18
0.0024	1.37	0.099	0.0057	1.05	0.23
0.0040	1.51	0.129	0.0114	1.37	0.29

as Table VI and shown in Fig. 4. The reason for taking these values from a graph is that it was not possible to make a series of mixtures that would all come to exactly the same equilibrium concentration of hydrogen ion. The reading off of values from the curves seemed to be the best method of interpolation. It will be noted that the effectiveness of the calcium approaches zero as the pH value decreases while that of sulfate increases with decreasing pH value.

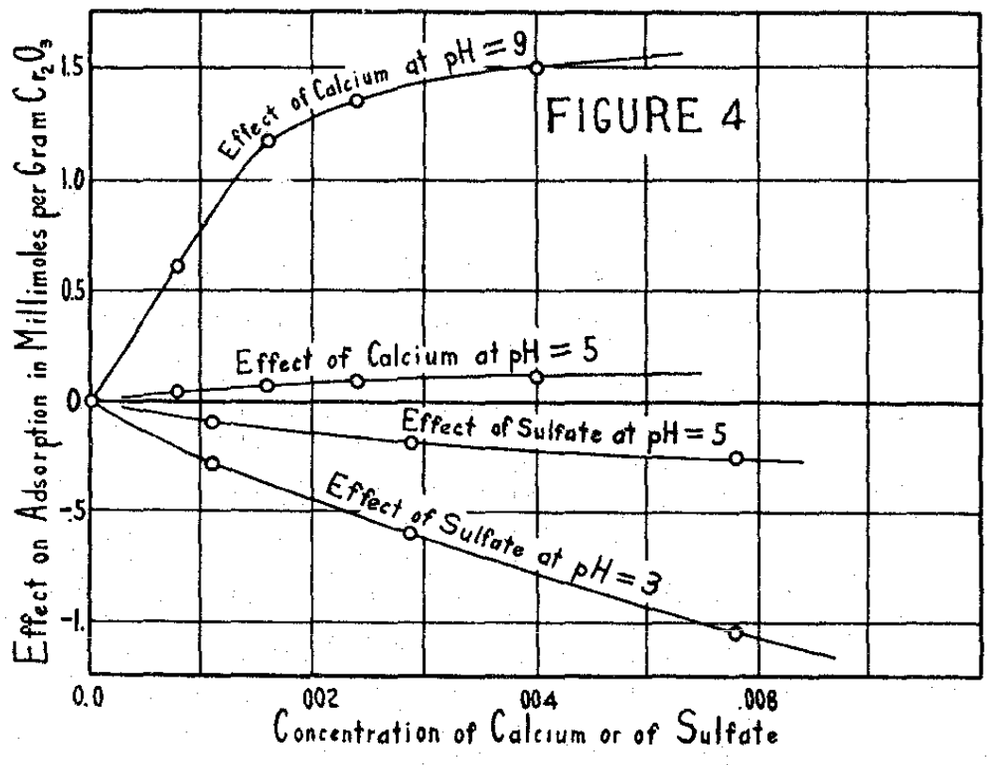
The Effect of Calcium Sulfate on the Adsorption of Alizarin SW at varying Hydrogen ion Concentrations. Since the foregoing experiments show that the effect of the sulfate is large in the acid and negligible in the basic baths and

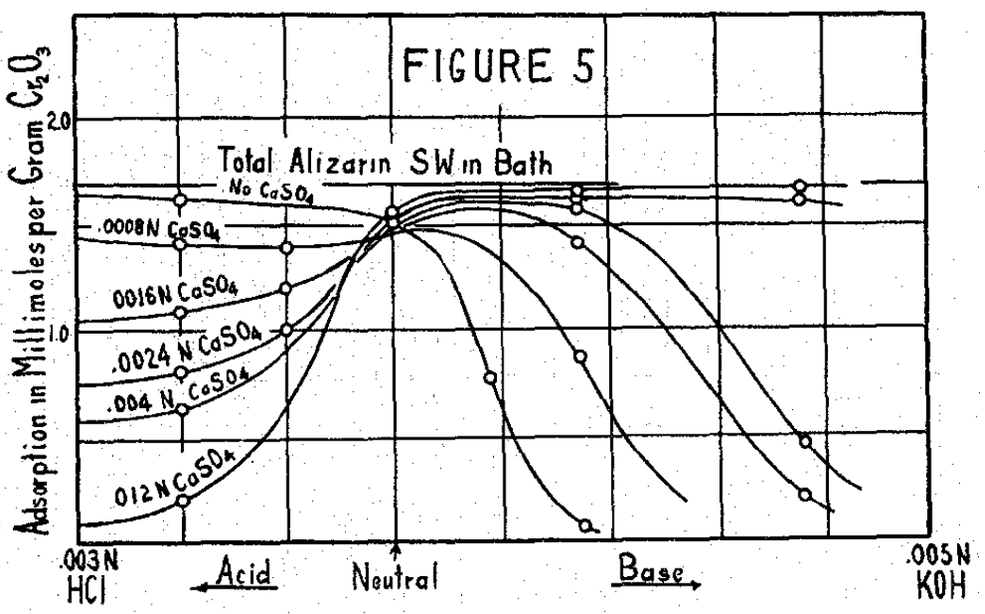
that the effectiveness of the calcium increases with the hydroxyl ion concentration, one is lead to conclude that if calcium sulfate were present the effect of the sulfate would predominate in the acid solutions and that the influence of the calcium would be unaffected by the sulfate in the basic baths. Direct experimental verification of this conclusion is given by the data recorded in Table VII and plotted in Fig. 5. If Figs. 2, 3, and 5, all of which are plotted

TABLE VII

Adsorption of Alizarin SW at varying pH Values in varying Concentrations of Calcium Sulfate

Cc of soln. mixed with 5 cc of sol containing 0.0125 gram of Cr_2O_3 in a total of 35 cc				Adsorption value in millimoles alizarin SW per gram C_2O_3	pH of mixture
0.04 N HCl	0.0274 N $CaSO_4$	0.037 N KOH	0.006 M dye		
2	0	0	5	1.62	2.606
1	0	0	5	1.58	3.000
0	0	0	5	1.52	4.212
0	0	1	5	0.77	8.321
0	0	2	5	0.06	9.174
5	1	0	5	1.43	2.207
2	1	0	5	1.40	2.606
1	1	0	5	1.38	3.002
0	1	0	5	1.44	5.158
0	1	2	5	0.78	8.611
0	1	5	5	0.03	10.441
5	2	0	5	1.13	2.129
2	2	0	5	1.09	2.522
1	2	0	5	1.19	2.825
0	2	2	5	1.40	8.619
0	2	5	5	0.26	10.385
5	3	0	5	0.92	2.174
2	3	0	5	0.80	2.494
1	3	0	5	1.00	2.803
0	3	0	5	1.39	5.967
0	3	2	5	1.57	8.202
0	3	5	5	0.41	10.280
5	5	0	5	0.56	2.146
2	5	0	5	0.63	2.501
0	5	0	5	1.47	5.122
0	5	2	5	1.61	8.386
0	5	5	5	1.62	9.815
5	15	0	5	0.27	2.396
2	15	0	5	0.20	2.931
0	15	0	5	1.53	4.176
0	15	2	6	1.63	8.351
0	15	5	5	1.67	8.807





on the same scale, are superimposed so that the adsorption curves in the absence of any salt coincide, 5 and 2 are alike in the acid range while 5 and 3 are alike in the basic range. These data show that the effects of the calcium and sulfate ions in the bath are practically independent of each other and that each is dependent on the hydrogen ion concentration.

The Effect of Calcium Ion and of Sulfate Ion on the Adsorption of Alizarin. Observations on the effect of calcium and sulfate ions on the adsorption of alizarate ion from a sodium alizarate bath are given in Table VIII and plotted in Fig. 6. Since the bath must be basic in order for the dye to remain in solution,

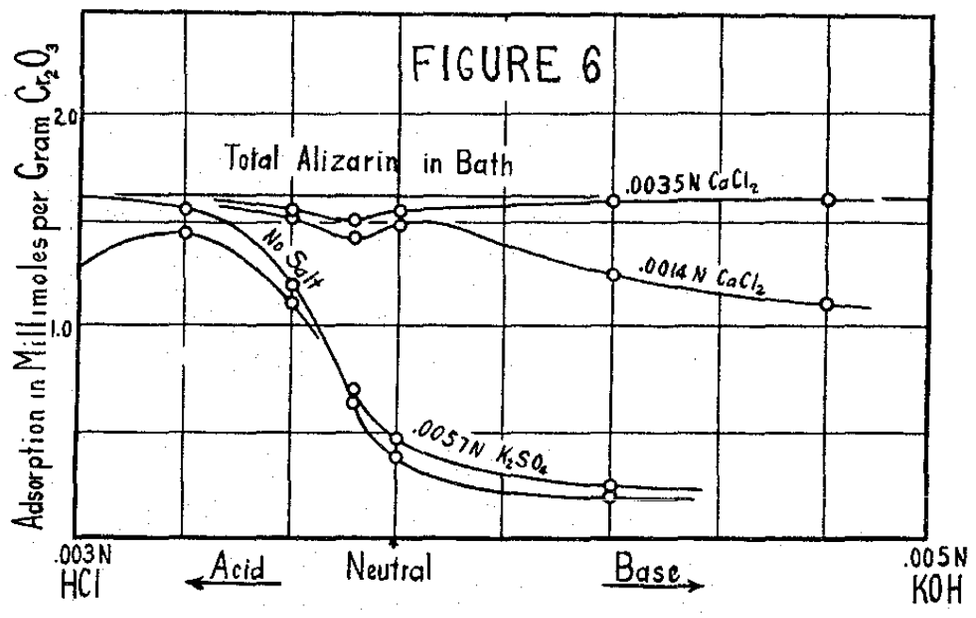
TABLE VIII

The Adsorption of Alizarin at different Calcium, Sulfate, and Hydroxyl Ion Concentrations

Cc of soln. mixed with 5cc of sol containing 0.0125 gram of Cr_2O_3 in a total of 35 cc.					Adsorption value in millimoles alizarin per gram Cr_2O_3
0.04 N HCl	0.02 N K_2SO_4	0.037 N KOH	0.003 M Alizarin	0.0244 N $CaCl_2$	
1.0	0.0	0.0	10	0.0	1.55
0.5	0.0	0.0	10	0.0	1.19
0.2	0.0	0.0	10	0.0	0.64
0.0	0.0	0.0	10	0.0	0.39
0.0	0.0	1.0	10	0.0	0.22
0.0	0.0	2.0	10	0.0	0.13
1.0	10	0.0	10	0.0	1.43
0.5	10	0.0	10	0.0	1.11
0.2	10	0.0	10	0.0	0.69
0.0	10	0.0	10	0.0	0.47
0.0	10	1.0	10	0.0	0.23
0.5	0.0	0.0	10	2.0	1.53
0.2	0.0	0.0	10	2.0	1.42
0.0	0.0	0.0	10	2.0	1.50
0.0	0.0	1.0	10	2.0	1.25
0.0	0.0	2.0	10	2.0	1.13
1.0	0.0	0.0	10	5.0	1.62
0.5	0.0	0.0	10	5.0	1.54
0.2	0.0	0.0	10	5.0	1.51
0.0	0.0	0.0	10	5.0	1.55
0.0	0.0	1.0	10	5.0	1.60
0.0	0.0	2.0	10	5.0	1.62
0.0	0.0	5.0	10	5.0	1.62

one would expect the effect of sulfate to be slight, as the observations show. On the other hand, the effect of calcium is marked and increases with its concentration. Hence by the addition of a strongly adsorbed cation one may use a slightly basic bath in which the alizarin is soluble and at the same time avoid the displacement of the dye anion by the hydroxyl. This is the function of

the calcium ion in the formation of alizarin lakes. That the effectiveness of the calcium is not due to the direct precipitation of calcium alizarate is evidenced by the fact that the quantity of calcium present may be greater than the equivalent of the alizarin without the dye bath becoming exhausted



Summary

1. A study has been made of the mechanism of the formation of alizarin lakes with the hydrous oxides of iron, chromium and aluminum and the influence of the concentration of the hydrogen ion and other ions on the lake formation process.

2. In every case lake formation is due to the adsorption of the dye anion by the hydrous oxides in varying amounts depending on the composition of the dye bath.

3. The influence of hydrogen ion concentration on the adsorption of alizarin SW is similar to that on sulfate and on oxalate. The order of adsorbabilities from the neutral and basic baths is alizarin SW > oxalate > sulfate.

4. The formation of alizarin lakes from sodium alizarate baths is due to adsorption of the dye anion by the hydrous oxide and not to the direct adsorption of the neutral sodium alizarate as suggested by Bull and Adams and by Williamson, or to double decomposition between the dye and the oxide as proposed by Biltz in the case of ferric oxide.

5. The effect of sulfate ion on the adsorption of alizarin SW is similar to its effect on the adsorption of oxalate, sulfate replacing the dye if the bath is acid. The power of the sulfate ion to replace the dye anion decreases to zero as the bath becomes alkaline.

6. The effect of calcium ion on the formation of alizarin lakes is to increase the charge on the mordant, thereby enabling it to adsorb more of the dye anion rather than to remove sulfate from the bath as suggested by Bancroft, or to form a complex calcium aluminum alizarate.

7. The salt effects in the mordanting processes may be summarized as follows:

(a) The presence of a strongly adsorbed cation in the dye bath increases the rate and quantity of adsorption of acid dyes and has an opposite effect on basic dyes, its effect increasing with the pH of the bath and with its own concentration.

(b) The presence of a strongly adsorbed anion in the dye bath decreases the rate and quantity of adsorption of acid dyes and increases the adsorption of basic dyes, its effectiveness increasing with the acidity of the solution and with its own concentration.

(c) If the dye bath is either acid or basic the effects of the cations and anions are practically independent of each other, the influence of the cation predominating in the basic bath and of the anion in the acid baths.

The above conclusions apply also to the dyeing of fibers in the absence of a mordant.

The Rice Institute,
Houston, Texas.

ADSORPTION BY METALLIC HYDROXIDES

Part V. A Comparative Study of the Adsorptive Power of Iron, Aluminium and Chromium Hydroxides for Acids and Alkali

BY KSHITISH CHANDRA SEN

From the experimental results already given in the previous papers, it will be observed that all these hydroxides show a great adsorptive power when acids or bases are used as the adsorbable solutes. No comparative study has however been made so far on the adsorptive power of these hydroxides. As the three hydroxides are very allied in their chemical and physical properties, a comparison of their adsorbing powers appears to be interesting, and as such the result of adsorption of acids will be given in the following tables.

Before however one can make some comparison, it is evident that the samples which has been used for the adsorption experiments should be comparable to each other. It has already been pointed out in previous papers, that the variation in the physical character of the adsorbent affects appreciably the amount of adsorption and it is reasonable therefore that the precipitates of the different hydroxides should be as similar as possible. This condition is however impossible to attain owing to the variability of the nature of the precipitate which is dependent upon a large number of factors. Attempt was therefore made to obtain what may be termed, average samples, which will give at least the general order of the adsorption values. All the three hydroxides were precipitated from the solutions of the chlorides of the respective metals by means of a slight excess of ammonia, and then freed from electrolytes by means of decantation and dialysis. The concentration of the chloride solutions was about 2N in each case, and the precipitation was always carried out in the cold. All the hydroxides were allowed to age for 25 days after which the adsorption was measured. Since the amount of adsorption was measured. Since the amount of adsorption calculated per gram adsorbent depends upon the actual amount of the adsorbent taken for the experiment, the amount of the three hydroxides used was kept almost the same. It will thus be observed that the adsorption values determined for the three hydroxides are fairly comparative. In Table I, the results obtained with the arsenious oxide are shown.

TABLE I

Original conc. of As_2O_3 in grams	Adsorption per gram		
	Cr_2O_3	Fe_2O_3	Al_2O_3
0.30	0.635	0.242	0.182
0.20	0.535	0.232	0.153

From Table I it will be observed that chromic hydroxide adsorbs arsenious acid much more than either ferric hydroxide or aluminium hydroxide does. Similar results have also been found in the case of sodium arsenite.

In Table II the results obtained with various mineral and organic acids are shown. It will be observed that in all these cases, hydrated chromium oxide has always the greatest adsorptive power, then comes ferric hydroxide, and aluminium hydroxide has the least adsorptive power among all these three. The only exception to this however is the case of sulphuric acid, where alumina shows a greater adsorptive power than ferric hydroxide.

TABLE II

Original concentration of acid 1.1320 milli equivalents per 100 cc.

Acid	Adsorption in milli equivalents per gram. of Cr_2O_3	Fe_2O_3	Al_2O_3
Citric	4.254	2.581	2.349
Racemic	4.212	1.917	1.904
Oxalic	4.295	2.065	1.866
Sulphuric	4.273	1.696	1.793
Malic	4.212	2.065	1.718
Succinic	4.056	1.659	—
Hippuric	4.037	1.512	—
Benzoic	3.920	1.402	—

From these results it is apparent that chromium hydroxide adsorbs acids much more than either ferric or aluminium hydroxide. Indeed the adsorptive power of chromium hydroxide is so high that 0.261 grams of Cr_2O_3 make 100 cc of 0.01N solutions of ordinary acids practically neutral to phenolphthalein. Under the same conditions 0.267 grams of Al_2O_3 takes up only 54 per cent of citric acid which is the most highly adsorbed by this substance, and 0.2559 grams of Fe_2O_3 takes up about 56 per cent of citric acid. These results therefore show the very high adsorbing power of hydrous chromium oxide. It must also be remembered that in order to get comparative result only 20 hours were allowed for the adsorption to take place. It has already been shown in the foregoing paper that increase in the time of contact appreciably increases the amount of adsorption by the chromium hydroxide while no such increase was observed in the case of hydrated iron and aluminium oxides. Hence if the time of contact would have been increased much more, hydrated chromium oxide would have shown a much higher amount of adsorption.

So long a comparative study of the adsorptive power of these hydroxides on acids has been made. When a similar study is made on the adsorption of alkali, it is observed that here also hydrated chromium oxide apparently adsorbs the highest amount of alkali. The adsorption by hydroxide alumina is almost equal to that of chromium hydroxide, but ferric hydroxide shows a much less adsorptive power. In studying these adsorptions no formation of sodium chromite or aluminate was observed. These results are thus a little different from that obtained in the case of acids. The amount of adsorption is no doubt dependent not only on the physical nature of the substance, but also on the chemical nature of the adsorbent.

Chemical Laboratory
Allahabad University,
Allahabad.

STUDIES ON GLASS

I. The Transition between the Glassy and Liquid States in the Case of Some Simple Organic Compounds

BY GEORGE S. PARKS AND HUGH M. HUFFMAN

This paper is the first of a series dealing with the nature of the glassy state. In it we are presenting some data which we have recently obtained in a study of the transition between the glassy and liquid states in the cases of normal propyl alcohol and propylene glycol. For a more complete consideration of the phenomenon involved we have also reviewed some recent investigations on ethyl alcohol and glycerol.

In the past a glass has been generally considered to be simply an undercooled liquid. As a consequence, the transition between the glassy and liquid states has been imagined as gradual and continuous. Thus, for instance, Nernst[1] has stated regarding a glass that "externally it has the properties of a solid, owing to great viscosity and considerable rigidity, produced by strong mutual action of the molecules. An amorphous body differs from a crystal, however, in its complete isotropy and absence of a melting point; on heating, it passes continuously from the amorphous to the usual liquid state, as its properties show steady change with rise of temperature, and no breaks anywhere."

Tammann's view is essentially similar, as the following quotation[2] will indicate. "The viscosity of a liquid increases with increasing undercooling, and in a rather narrow temperature interval it increases very rapidly to values characteristic of solid crystals. A brittle glass is thus formed from an easily mobile liquid. This change in viscosity does not correspond to the behavior of the other properties, which in this temperature interval change relatively only slightly. The change in viscosity is a continuous one and no temperature can be chosen as the freezing-point, the point at which the liquid becomes solid. *Glasses are undercooled liquids.*"

By our own studies upon the transition of organic glasses into the corresponding liquids we have been led to a somewhat different conclusion. While there is no definite temperature, comparable to the melting point of a crystal, at which all properties undergo a sharp change, there is nevertheless a temperature interval, definite and reproducible, in which a number of properties change with a rapidity approaching that observed in the case of the melting process of a crystal. In brief, there is a softening region instead of a melting point. The glass as it exists below this softening region differs so markedly from the liquid existing above that it might well be considered as a different state of the substance. For this reason we have recently suggested the

[1] Nernst (translation by Tizard): "Theoretical Chemistry," 94 (1911).
[2] Tammann (Mehl): "The States of Aggregation," 3 (1925).

possibility of regarding glass as a fourth state of matter,[1] distinct from both the liquid and crystalline states and yet showing to some extent characteristics of both these states. A promising alternative hypothesis involves the view that it is a colloid very much analogous to a jelly. According to this last explanation the softening region represents the temperature range through which the jelly changes into an associated liquid.

At any rate, whatever be the true explanation, we feel that the data which we consider in the following sections of this paper are indicative of a distinct and fundamental difference between the glassy and liquid states.

Heat Capacity Data

Many organic compounds, especially those containing one or more hydroxyl groups such as the alcohols and sugars, can be converted from the liquid to the glassy condition by cooling. In some cases, that of ethyl alcohol for instance, the cooling process must be carried on rapidly by means of liquid air to prevent crystallization. In other cases the glass appears to be extremely stable and can be formed either by slowly cooling or rapidly cooling, as suits the desire of the investigator; propylene glycol is an instance of the latter type.

When a simple alcohol glass, such as that of glycerol, is heated its heat capacity at first increases gradually with the temperature in much the same fashion as in the case of the crystalline form. Eventually, however, a temperature region is reached in which the specific heat of the material is almost doubled within an interval of only 10°. A maximum point is then attained and thence the heat capacity drops off slightly with increasing temperature to give the curve for the liquid state. We thus find two distinct, continuous specific heat-temperature curves, one for the glass essentially similar to that for the crystalline material and one for the liquid. Between the two there is a transitional region existing over a temperature interval of 10° to 20°.

This phenomenon was first studied by Gibson, Parks and Latimer[2] in the case of the glasses of ethyl and n-propyl alcohols. Later a similar behavior was observed separately by Simon[3] and by Gibson and Giauque[4] for glycerol glass. More recently Parks[5] has repeated the work in the case of ethyl alcohol. In the present investigation we have obtained new results for n-propyl alcohol and also fairly extensive data on propylene glycol. Thus we now have available specific heat data for four related compounds in the glassy state.

Materials.—The n-propyl alcohol employed in the present investigation was prepared from Eastman's "refined" product by treatment and distillation with lime in the ordinary manner. The resulting material was carefully fractionated and the middle third was selected for use in the measurements. It had a boiling range of 0.05° and a density of 0.8010 at 25°/4°.

[1] Parks and Huffman: Science, **64**, 364 (1926).
[2] Gibson, Parks and Latimer: J. Am. Chem. Soc., **42**, 1547 (1920).
[3] Simon: Ann. Physik, **68**, 260 (1922).
[4] Gibson and Giauque: J. Am. Chem. Soc., **45**, 93 (1923).
[5] Parks: J. Am. Chem. Soc., **47**, 341 (1925).

The propylene glycol was a high-grade material, obtained from the Special Chemicals Company. It was carefully fractionated by distillation at a pressure of 4 mm. and a temperature of about 73° C. The resulting middle fraction, which had a density of 1.0493 at 25.8°/4°, was used for the present work.

Method.—In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" or instantaneous specific heats. A measured amount of heat was supplied by an electric current to the substance contained in a copper calorimeter, which was suspended in a vacuum and surrounded by a silvered copper cylinder in order to diminish the conduction and radiation of heat to and from the surroundings. A thermocouple in the center of the calorimeter measured the rise in temperature. The entire apparatus and details of experimental procedure have been fully described in other places.[1]

In view of the accuracy of the various measurements involved, the error in the experimental values thereby obtained is probably less than 1%, except in the transition interval. In this particular region the errors may be considerably larger than this value, owing to uncertainty in the attainment of thermal equilibrium and also to incipient crystallization in the case of the propyl alcohol. However, all cooling corrections were made in a uniform manner and hence the specific heat results should be comparable throughout, altho there may be some uncertainty as to the absolute values.

TABLE I

Specific Heats of Ethyl Alcohol Glass and Liquid

Temp., °K.	Cp per gram	Temp., °K.	Cp per gram
86.8	0.264	110.2	0.415
87.5	0.266	160.0	0.455
88.1	0.263	200.0	0.468
90.8	0.296	240.0	0.496
91.9	0.301	250.0	0.507
95.8	0.420	275.0	0.543
97.5	0.443	290.0	0.572
100.5	0.423	298.0	0.588
105.5	0.399		

TABLE II

Specific Heats of N-Propyl Alcohol Glass and Liquid

Temp., °K.	Cp per gram	Temp., °K.	Cp per gram
86.4	0.233	169.1	0.430
91.5	0.255	185.9	0.438
96.0	0.333	193.5	0.441
100.0	0.46	197.7	0.444
103.7	0.426	201.6	0.447
108.0	0.425	275.1	0.531
112.6	0.424	275.3	0.531

[1] Parks: J. Am. Chem. Soc., **47**, 338 (1925); also Parks and Kelley: J. Phys. Chem., **30**, 47 (1926).

Results.—The data which we have obtained in the present investigation appear in Tables II-V. For a complete treatment of the subject and for purposes of comparison we have also included Parks' data on ethyl alcohol (Table I) and representative values from the results of Gibson and Giauque for glycerol (Table VI). The 15° calorie is employed throughout.

TABLE III

Specific Heats of Propylene Glycol Glass and Liquid (Determinations made after formation of the glass by cooling from 250° to 90° K. in approximately 1 hour.)

Temp., °K.	Cp per gram	Temp., °K.	Cp per gram
91.1	0.1631	160.3	0.3747
97.9	0.1721	164.1	0.48
104.5	0.1802	167.1	0.4641
111.0	0.1882	172.6	0.4649
122.6	0.2025	177.8	0.4664
128.5	0.2099	187.2	0.4689
133.9	0.2166	196.9	0.4758
139.1	0.2223	274.8	0.5658
144.2	0.2314	275.8	0.5660
149.2	0.2392	276.3	0.5671
153.3	0.2517	276.6	0.5665

TABLE IV

Specific Heats of Propylene Glycol Glass and Liquid (Determinations made after formation of the glass by cooling from 200° to 136° K. in approximately 50 hours.)

Temp., °K.	Cp per gram	Temp., °K.	Cp per gram
141.3	0.2240	173.5	0.4658
147.1	0.2317	183.8	0.4695
152.4	0.2447	194.3	0.4748
160.0	0.4024	199.8	0.4796
163.4	0.48	204.6	0.4813
168.2	0.4642		

TABLE V

Specific Heats of Propylene Glycol Glass and Liquid (Determinations made after formation of the glass by cooling rapidly as in Table III.)

Temp., °K.	Cp per gram	Temp., °K.	Cp per gram
132.7	0.2145	153.5	0.2512
139.6	0.2235	160.4	0.3671
146.1	0.2359	163.8	0.48

The results contained in Tables I, II, III and VI are shown graphically in Fig. 1. It is clear that the specific heat-temperature curves for these four glasses are remarkably similar, differing from one another largely by a shift along the temperature axis. The two alcohols which possess one hydroxyl group per mol, ethyl and n-propyl alcohols, show the sudden transition in specific heat in practically the same temperature range (90°-100° K.), altho in the case of the former the data are somewhat scanty and uncertain due to the comparatively great tendency toward crystallization. When a second OH group is introduced into the n-propyl alcohol molecule, thus giving propylene glycol, the transition is raised to 153°-165°. The introduction of a third hydroxyl produces glycerol with the jump at 180°-190°. In the case of glucose, an aldehyde-alcohol containing five hydroxyl groups, we have recently found

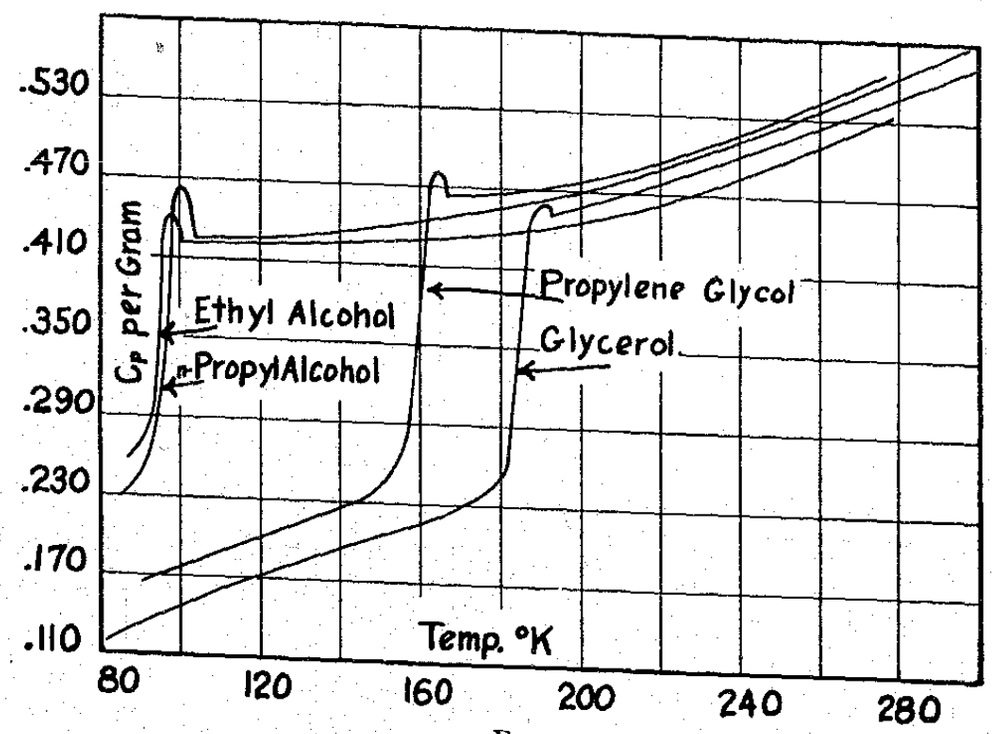


FIG. 1

TABLE VI

Specific Heats of Glycerol Glass and Liquid

Temp., °K.	Cp per gram	Temp., °K.	Cp per gram
70.2	0.1116	173.4	0.2338
82.1	0.1260	179.8	0.2467
93.9	0.1420	187.4	0.4325
104.1	0.1542	191.6	0.4603
115.3	0.1644	192.6	0.4556
125.6	0.1730	203.7	0.4633
135.9	0.1834	218.7	0.4775
148.8	0.1981	240.1	0.5026
165.0	0.2181	275.4	0.5431
		299.4	0.5795

that the transition comes suddenly at 275° -290°. Evidently increasing the number of OH groups in the molecule raises the temperature of the "jump."

It occurred to us that the character of this "jump," as well as the temperature at which it takes place, might also be influenced to some extent by the previous history of the glass. For this reason we have carried out the determinations (Tables III, IV and V) on propylene glycol after rapidly cooling, slowly cooling, and again rapidly cooling. The results seem to indicate that the process of slowly cooling gives a sharper rise during the transition and values about 1% lower for the specific heat of the glass. The character of the cooling seemed to have no influence upon the specific heat values at temperatures above the jump. These findings are also represented graphically in Fig. 2.

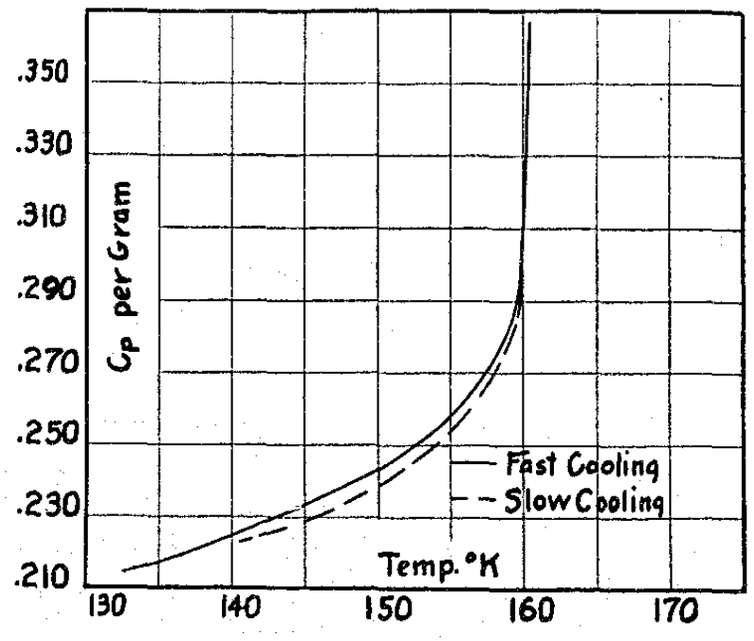


FIG. 2

As Tammann points out (p. 247), "the viscosity of a liquid at first increases slowly with increasing undercooling and then reaches a critical temperature, at which the rate of increase mounts rapidly until finally a hard, brittle glass is formed. Quantitative measurement of the change in viscosity during undercooling has shown that although the viscosity increases very rapidly, though continuously, with falling temperature, that is, with an increasing rate of change, other properties show no variations in rate during the formation of the brittle glass. For example, the expansion coefficient for betol or piperine shows no change during this abnormal increase in viscosity."

While we have not personally investigated the two substances just mentioned, we are inclined to feel that the preceding quotation is by virtue of its implications somewhat misleading, for we have just seen that there is a sharp change in specific heats during the transition between the glassy and liquid states. It is true, this change does not come *exactly* at the temperature of rapid increase in viscosity but certainly the two phenomena are so near to one another on the temperature scale as to immediately suggest a close and

fundamental relationship. However, the point that we wish to bring out at the present time is that on heating a glass the material softens very rapidly within a comparatively small temperature interval to give a viscous liquid. In the cases of propyl alcohol, propylene glycol, and glycerol we have roughly determined this softening or "melting" temperature by immersing a thermocouple, contained in a small Pyrex tube, in a sample of the alcohol and then chilling to produce the glass. The material was thereupon allowed to warm up gradually and the first or lowest temperature at which the thermocouple tube could be moved or turned within the alcohol glass was taken as the approximate softening temperature. These temperatures were respectively 107°, 185° and 221° K., or in other words about 7°, 20° and 31°, respectively, above the maximum point for the jumps in the specific heat curves for n-propyl alcohol, propylene glycol and glycerol. Thus, on heating up the glass, the softening phenomenon becomes noticeable after the sudden increase in heat absorption and not during it.

Expansion Data

Most inorganic glasses show a definite and rather abrupt change in the coefficient of expansion[1] as the softening region is approached. In the case of commercial glasses, owing to their varied and complicated character, the significance of this phenomenon has been obscure. However, very recently data on a chemically simple inorganic glass, B_2O_3, has been obtained by Tool and Valasek[2] and by Samsoen.[3] On heating up this oxide, the former found evidence of a marked heat absorption from approximately 240° to 285° C.; their work was purely qualitative. Subsequently Samsoen observed a sharp twelve-fold increase in the coefficient of expansion of this substance at about 245° C. Moreover, he and Mondain Monval[4] found that the heat absorption came abruptly at about 217° C. and that the specific heat of the compound above this temperature was 14% greater than below it. None of these investigators state the temperature of the softening point but we ourselves have located it at about 400° C by means of a calibrated chromel-alumel thermocouple. Thus it appears that in the case of this simple inorganic glass there is first a region of heat absorption and sharp rise in specific heat at about 217°, then a twelve-fold change in the coefficient of expansion at about 245° and finally the attainment of a definite condition of softness or fluidity above 400° C.

In the present investigation on organic glasses we have observed the heat absorption and sharp change in specific heat at from 7 to 31 degrees below the point at which softening becomes appreciable and, in order to test further the analogy with inorganic glasses, we have been very desirous of obtaining data on the coefficient of expansion of the alcohols under consideration. However, the experimental difficulties attending such measurements appear to be very

[1] Peters and Cragoe: Bur. Standards Sci. Paper, **16**, 449 (1920).
[2] Tool and Valasek: Bur. Standards Sci. Paper, **15**, 537 (1919).
[3] Samsoen: Compt. rend., **181**, 354 (1925).
[4] Samsoen and Mondain Monval: Compt. rend., **182**, 968 (1926).

great, as we are really dealing with a solid at the lower temperatures and with a liquid above the softening region. Hence a method which is applicable to a solid only or to a liquid only does not meet the present requirements. As a consequence of these difficulties the method which we have devised and are about to describe leaves much to be desired. It is, nevertheless, the one which seemed most feasible for measurements on glasses at the low temperatures involved.

A cylindrical, Pyrex dilatometer of about 25 cc capacity, equipped with a heating-coil and a copper-constantan thermocouple, contained the alcohol sample. From the top of this cylinder, which was about 10 cm. long, a capillary tube led to an adjoining mercury manometer. Connection between the capillary tubing and the manometer was made by a vacuum-tight de Khotinsky seal. At a distance of 1 to 2 mm. the dilatometer was surrounded by a cylindrical copper jacket, also supplied with a heating-coil and thermocouple for temperature regulation. The whole was then suspended in a larger brass can or container, equipped with a top which could be soldered into place and made vacuum tight. A German-silver tube 1 cm. in diameter and 40 cm. long, brazed into this top, served the three-fold purpose of connecting the system to the charcoal evacuating tube, of providing an exit path for the electrical connections and the capillary tube to the manometer and of acting as a support, the entire apparatus being suspended in a 1000 cc Dewar jar. Details of electrical wiring, of temperature measurement, etc., were essentially the same as those employed in the determination of specific heats and need not be repeated here. Satisfactory thermal insulation of dilatometer and jacket from the outer brass can was obtained by a vacuum produced by a preliminary evacuation with a Nelson oil-pump, followed by the use of activated charcoal immersed in liquid air. During all the measurements on the n-propyl alcohol and propylene glycol a bath of liquid air was maintained in the surrounding Dewar vessel. The dilatometer and its copper jacket could then be adjusted to and maintained at higher temperatures by means of the respective heating coils and thermocouples.

The actual procedure in making the measurements was as follows. The calibrated dilatometer was almost completely filled with the substance under investigation, about 1 cc of space being left for the air which served as the dilatometric fluid. It was then put in place with the surrounding copper jacket and connected up with the mercury manometer. After cooling with liquid air and the subsequent evacuation of the surrounding brass can, the pressure of the air within the dilatometer was obtained by reading the manometer. The dilatometer and contents and the copper jacket were then heated up a definite temperature interval of 5 or 10°. After the lapse of sufficient time for the attainment of thermal equilibrium the manometer reading was again taken. On the assumption that the adsorption of the air by the alcohol sample is negligible or at least uniform, the increase in the pressure of the air in the dilatometer is the result of two factors: (1) the increase in the temperature of the air sample, and (2) its decrease in volume due to the increase in volume of the alcohol sample. By assuming the perfect gas equation for the

air sample, we can thus calculate its volume at a series of ascending temperatures. In each case the volume of the alcohol sample is then simply the difference between the total volume of the Pyrex dilatometer and the corresponding volume occupied by the air.

For propylene glycol we have made by this method four series of determinations, one of which is represented by the results in Table VII.

TABLE VII

Dilatometer Data on Propylene Glycol, Series 2

Temp., °K. T	Pressure of air sample, P	$\frac{dP}{dT}$	Volume of glycol sample, V	Coefficient $\frac{1}{V}\left(\frac{dV}{dT}\right)$
122.6	269.1 mm.		22.89 cc	
		2.5		
131.1	290.7 "		22.92 "	
		2.5		
140.1	313.9		22.96	
		2.4		
150.5	338.6		22.98	$1.4(10^{-4})$
		2.6		
160.2	363.4		23.01	
		2.5		
165.2	376.0		23.02	
		2.8		
170.0	389.5		23.04	
		4.4		
175.0	411.5		23.13	
		4.8		
180.0	435.9		23.23	
		4.3		6.4 "
185.1	457.9		23.30	
		4.1		
190.2	478.9		23.35	
		4.5		
200.1	523.5		23.47	
				6.2 "
297.7	1439.3		24.88	

From these data it is apparent that above 170° K. there is a marked increase in dP/dT for the air sample and consequently in the coefficient of expansion of the glycol. Similar results were obtained in the other three series, altho in one case our dilatometer broke before we had made all the essential measurements. The values calculated for the three completed runs are summarized in Table VIII.

TABLE VIII
Coefficient of Cubical Expansion of Propylene Glycol

Series	Temperature Range, °K. 120°-170°	170°-200°	200°-298°
1	2.6×10^{-4}	7.1×10^{-4}	6.7×10^{-4}
2	1.4 "	6.4 "	6.2 "
3	2.0	5.4	5.7
Mean	2.0	6.3	6.2

These three series all agree in showing a marked increase in the coefficient of cubical expansion above 170°K., altho they do not yield the same numerical value for this quantity. Hence, it is apparent that the results obtained are merely qualitative. This situation may be due to error on our part in assuming that the adsorption of air by the alcohol sample was either negligible or uniform; in fact, it is quite possible that we are primarily measuring the change in such adsorption with temperature rather than the coefficient of expansion of the alcohol. At all events, the data are certainly indicative of a marked change in some property of the alcohol at about 170°.

We have also applied the method to the n-propyl alcohol glass but in this case we have observed no sharp change in the coefficient of expansion. However, as the transition between the glassy and liquid states actually starts at about 90° K. and our manometer readings did not go below this temperature, such a result is not really surprising and does not constitute proof of the non-existence of a change.

In the case of glycerol Samsoen[1] has employed a crude dilatometric method, in which a "semi-capillary" tube was used and the glycerol itself played the part of the dilatometric fluid. His measurements show an abrupt doubling of the coefficient of expansion at 211°K.

Thus, in the case of the two alcohols which have been studied in both the glassy and liquid states over a wide range of temperatures we have some evidence of an abrupt change in the coefficient of expansion at a point intermediate between the "jump" in the specific heat curve and the "melting" temperature.

Thermal Conductivity

The time required for the attainment of thermal equilibrium in the course of a specific heat determination constitutes a rough inverse measure of the thermal conductivity of the substance at the temperature in question and may also serve to indicate the existence of a transition region involving the absorption of heat. On this basis we find that these substances in the glassy state are reasonably good conductors of heat; in fact, they have a thermal conductivity approximately equal to that of a crystalline organic compound. In the specific heat determinations on propylene glycol glass, for instance, thermal equilibrium was invariably attained in about 4 minutes after cessation of the heating current. After the material became definitely liquid, altho

[1] Samsoen: Compt. rend., **182**, 518 (1926).

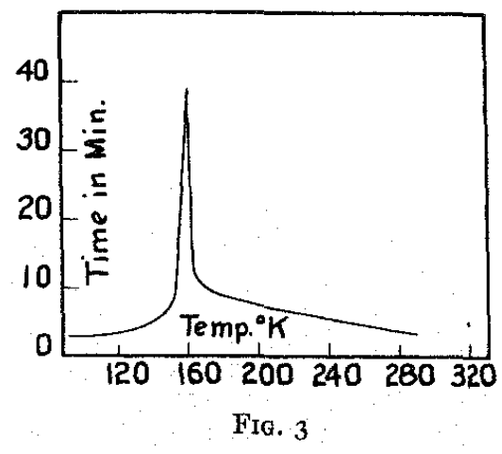


FIG. 3

very viscous, the conductivity was again good and thermal equilibrium was attained in about 7 minutes. However, in a portion of the transitional region between the glassy and liquid states, the attainment of thermal equilibrium took much longer—in fact, 39 minutes at 160° K. This situation is represented graphically in Fig. 3 where the time required for thermal equilibrium in the propylene glycol runs has been plotted against the corresponding temperatures. A similar phenomenon has been observed in the case of the three other alcohols.

Dielectric Constant

For glycerol Fleming and Dewar[1] observed the change in dielectric constant on cooling the liquid down to the glassy condition. Their results, which are represented graphically in Fig. 4, show a slightly increasing value for the

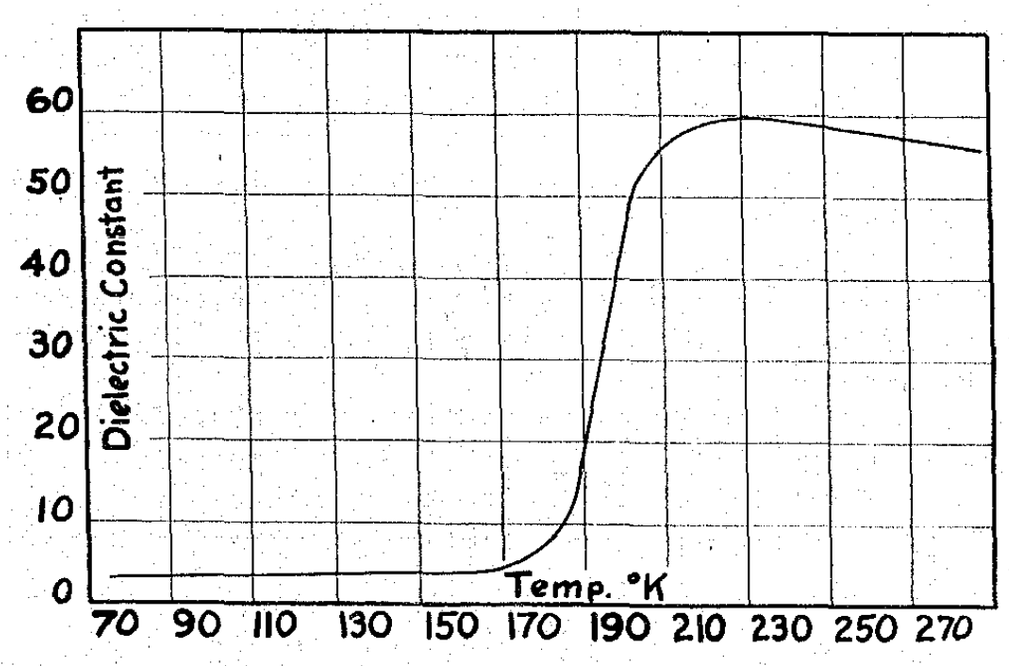


FIG. 4

dielectric constant as the liquid is first cooled. In the transitional region this quantity then decreases rapidly, reaching a very low figure as the glassy condition is attained. In this last state the value is of the same order of magnitude as that for crystalline substances, such as ethylene dibromide.

Summary and Discussion

Before proceeding to a discussion of the glassy state, it seems to us desirable to summarize the information which we have obtained in the study of these alcohols. Apparently in the glassy state these substances have almost

[1] Fleming and Dewar: Proc. Roy. Soc., **61**, 324 (1897).

the same values for heat capacity, thermal conductivity and dielectric constant as in the crystalline condition; furthermore, the values for heat capacity, thermal expansion and dielectric constant are very different from those observed for the liquid state. On the other hand, while the crystalline and liquid states are marked off from one another by a definite temperature, the melting point of the crystalline material, the transition between the glass and liquid is more indefinite. Instead of a mere point, there seems to be a transitional range of temperature in which there occurs a relatively great and rather abrupt change in specific heat, viscosity, coefficient of expansion, dielectric constant, and perhaps many other properties. What we have termed the softening or "melting" temperature may be considered as the upper boundary of this transitional range; the lower seems to be the temperature at which the specific heat of the glass starts to rise very suddenly. The whole interval thus defined amounts to about 17° for n-propyl alcohol, 30° for propylene glycol and 40° for glycerol, altho the change in any one property, such as specific heat, takes place within a much smaller range.

For these facts there are several possible explanations. According to one hypothesis which we have advanced, glass may be regarded as a fourth state of matter, distinct from the liquid and crystalline states and yet showing to some extent characteristics of both these states. A liquid is characterized by a *random, haphazard arrangement* of its component molecules or units and by *mobility*, due to the existence of variable, mobile forces between these units; while a crystal possesses *rigidity* and a *definite, orderly structure*. A glass, like a liquid, possesses a *random arrangement* of its units; on the other hand, like a crystalline substance, it has the property of *rigidity*. Because they are alike in this latter respect, the glass and crystalline states have nearly the same heat capacity. Furthermore, the comparatively large heat absorption in the case of the glass prior to the softening process is analogous to the heat of fusion in the melting of a crystalline material; in both cases the energy is required for breaking up a rigid structure. On the other hand, because it is irregular and random, the whole of the structure in a glass does not lose rigidity at exactly the same temperature; hence, the "melting" of a glass is not sharp and invariable as in the case of a crystal. Moreover, the quantity which we might term the heat of fusion of the glass proves to be smaller than the heat of fusion of the crystal. Thus, if we extrapolate the specific heat curve for the glass up to the softening or "melting" temperature and consider the excess heat represented by the actual curve in the transition region over this extrapolated curve as the heat of fusion, we obtain 1.96 and 7.19 cal. per gram, respectively, for n-propyl alcohol and glycerol. The heats of fusion for these substances in the crystalline form, calculated for the same temperatures by Kirchhoff's rule, are respectively 14.42 and 32.38 cal. per gram.

A second hypothesis which we have entertained is that glass is essentially a colloid similar to a jelly. This view seems reasonable, as well-made, typical jellies are optically clear.[1] According to this hypothesis the transition region

[1] McBain: Kolloid-Z., **40**, 1 (1926).

between the glass and liquid represents the temperature range in which the jelly is broken up and converted into an associated liquid or, perhaps, a sol. Of course, the ordinary colloid system consists of two phases, the dispersed phase and the dispersing medium, and involves at least two chemical compounds or components, while in the present case we have but one component —an *isocolloid*. However, it is even conceivable that here we have a situation in which the one component (i.e. the alcohol in question) exists in two or more forms and serves as both the dispersing medium and the dispersed phase. If this be true, it is a further possibility that equilibrium between the two phases is "frozen" by the use of relatively low temperatures in the same sense that the attainment of equilibrium appears to be upset by extreme drying, as illustrated in the work of Baker.[1] Assuming for the present discussion that glass is colloidal in character, we next face a question as to the nature of the aggregates or micells contained therein. These may be entirely amorphous, and probably are such in the case of many glasses, especially those involving a complicated chemical composition. On the other hand, in some instances they might be micro-crystalline particles. Wyckoff and Morey,[2] for example, in X-ray diffraction measurements on some soda-lime-silica glasses found indications but not positive proof "that entirely clear and apparently homogeneous glasses may contain large amounts of crystals of colloidal dimensions." We ourselves have noticed in the case of n-propyl alcohol that the glass upon heating up started to crystallize at practically the same temperature, about 127° K., on every occasion and Samsoen[3] has observed a similar phenomenon around 250° K. in connection with his studies on glycerol glass. These observations may be considered as circumstantial evidence of the existence of crystalline nuclei or aggregates within the solid glass, altho they can also be reconciled with the idea of amorphous aggregates.

Still another explanation would involve the possibility of a connection between these organic glasses and what Friedel calls the mesomorphic states of matter,[4] i.e. the so-called "liquid crystals," altho it is extremely doubtful whether these glasses are anisotropic. Moreover, there is this decided difference. The mesomorphic states are formed from the crystalline and exist within a temperature region intermediate between that of the crystalline and liquid forms, while these organic glasses are all formed by undercooling the liquid and exist at temperatures decidedly below the melting point of the crystalline form. Furthermore, at all temperatures the glass is really unstable in the presence of the corresponding crystals.

At the present time these several explanations are purely hypothetical and it seems to us undesirable to attempt to choose between them on the basis of data for only two or three properties. In this sense our present study is merely preliminary. We are now continuing it in the form of a broad and searching investigation of the properties of glucose (dextrose) in both the

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[1] Baker: J. Chem. Soc., **121**, 568 (1922).

[2] Wyckoff and Morey: Trans. Soc. Glass Tech., 9, 266 (1925). See also Scherrer: Zsigmondy's "Kolloidchemie," 407 (1920).

[3] Samsoen: Compt. rend., **182**, 846 (1926).

[4] See Jerome Alexander's "Colloid Chemistry," **1**, 102-126 (1926).

glassy and liquid states and in the intermediate transition region. In this connection we have already obtained most interesting and promising data.

Before concluding this paper we wish to thank Professor James W. McBain for the encouragement and advice which he has so generously given us in this investigation.

Department of Chemistry,
Stanford University, California,
July 9, 1927.



236

STRUCTURAL COLORS IN INSECTS. III

BY CLYDE W. MASON[1]

Iridescent Integuments

Because of their smooth, relatively uninterrupted surfaces and brilliant reflections iridescent integuments are likely to appear distinctly metallic, and the main question has been whether their lustre and colorings were due to selective reflection (such as is shown by colored metals and solid dyestuffs) or to thin films.[2] The highly metallic lustre which is so common among certain of Coleoptera is cited as evidence for the first view, while the very marked change of hue with increasing incidence supports the second explanation.

The examination of integuments of beetles and other insects is essentially similar to that of iridescent scales, except for the difficulties introduced by the underlying tissue and the heavier pigmentation which is usually present. The surfaces are larger, reflection and polarization may be studied more easily, and there is almost complete absence of striae or other structural features which might interfere with such observations. On the other hand, the color-producing layer is not easily accessible from the under side or by means of sections, and it is practically impermeable to liquids, besides being so hard as to be relatively resistant to mechanical deformation. However, the criteria enumerated in the study of iridescent scales may be applied with slight modifications to the specimens described below.[3]

Two main types of iridescent integuments may be recognized: "*metallic*," as shown by "blue-bottle"flies, and other less familiar insects; and "*enameled*," best exhibited by certain of the Cetonids.[4]

"Metallic" Integuments

In most respects iridescence of the "metallic" type shows the same features on whatever insect it may occur; the characteristic lustre and highly specular reflection are very distinctive. This is dependent on the smoothness of the surface, which is commonly almost perfectly even in small areas under the microscope. To the naked eye grosser structures such as ridges, "dimples,"

[1]The investigation upon which this article is based was supported by a grant to Messrs. Bancroft, Chamot and Merritt from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[2]Biedermann's paper [Handbuch der verg. Physiol., **3**, I, Part *2*, 1657 (1914)] gives a very complete discussion of the earlier work along this line, with various arguments for and against the different opinions.

[3]Nearly all of the specimens studied in the present paper were furnished through the kindness of Dr. W. T. M. Forbes and Mr. F. C. Fletcher, of the Department of Entomology at Cornell. The writer's ignorance of entomology would have handicapped him seriously if the advice and criticism of these gentlemen had not been available.

[4]Biedermann deals chiefly with the latter type. Michelson(Phil. Mag. (6) **21**, 564 (1911)) apparently studied only metallic integuments. Onslow (Phil.Trans. **211 B**, 1 (1921)) has considered both "metallic" and "enameled" iridescence.

fissures, and processes, even though completely covered with the color-producing layer, may prevent the high degree of reflection obtainable from a flat surface, with a resultant dulling of the color. Under these circumstances, because there is some small portion of the surface in position to reflect specularly at any angle, the reflection may be observed through a wide range, and the lustre, instead of being highly metallic, is more matte.[1] Under the microscope at low magnifications the "high-lights" of such an embossed or convoluted surface may be clearly seen, and the true specular character of the reflection recognized.

Lytta vesicatoria (*Meloidae*) is typical of a large variety of insects, as regards its structural and optical properties. The deeply convoluted surfaces of its elytra show a polygonal pattern which marks off the portions of the cuticle secreted by individual underlying cells. The color is localized in this cuticle, as shown by scraping; fragments of the color-producing layer may be removed by this means, and studied separate from the underlying deeply pigmented layer. Sections give some evidence of lamination in the cuticle, but this is not trustworthy on account of diffraction patterns and the possibility of spurious images.

Although the coloring appears substantially uniform to the eye, this is not the case under the microscope, for the green reflection, which is the predominating color, shades into bronze green or blue green in a very small space. This is partly due to the variation in shape of the surface, which results in different portions being observed at slightly different angles of incidence. The reflection color may be observed from the under side by scraping away the underlying tissues of the elytron. It presents the same appearance as from above.

The color of different insects varies in a manner similar to the local variations on the elytron; specimens in the collection range from bronze to greenish blue. This same variation may be seen with the naked eye on different parts of a single insect.

By transmitted light no color other than the brown of the pigment is observable. Scrapings from the outer surface are somewhat pigmented, but show no transmission color, other than this pale neutral brown.

Prolonged bleaching in strong hydrogen peroxide (10%) destroys the pigment without damaging the iridescent coloring; the elytra may be a very pale straw color by transmitted light with undiminished reflection color.

The change of hue with variation in the angle of incidence is most striking when a small flat portion of the surface is observed under a microscope; the change is evident enough but is somewhat less spectacular if the whole insect is observed with the naked eye. From bronze green, or even yellowish green, at normal incidence the color changes through green and blue to violet and may go as far as purple. If the insect is copper-red or bronze to the naked eye, it will ordinarily pass through the above series only as far as greenish

[1] This is exactly analogous to the behavior of metals, which darken as the surface is roughened, and which show a reflection scattered over a considerable angle when thus broken up into a great number of minute reflecting surfaces.

blue, while if it is bluish green at normal incidence the purple at grazing has a very distinct reddish cast. The *effective* angle of incidence may be considerably increased by placing on the elytron a drop of water or other liquid which does not spread to form a film but stands up with a highly convex surface. This corresponds to the prism arrangement frequently used for viewing Newton's rings,[1] and prevents the critical angle of the specimen from limiting the angle at which light can penetrate its surface.

The reflected light may be analyzed by a nicol prism, and shown to have properties similar to those exhibited by the scales of *Urania*, in that it is elliptically polarized, and, for angles greater than about 60°, the vibrations in the plane of incidence are of color complementary to those perpendicular to the plane of incidence, or to those of unpolarized light.

Swelling reagents affect the color very markedly. Steam, ammonia, phenol vapor, water, alcohol and many other liquids all bring about the same sort of color change; of these water (because of its chemically neutral character) and phenol vapor (because no liquid is brought in contact with the specimen) are preferable. In the case of *Lytta vesicatoria* the action of the swelling agent is more rapid (water, 10-15 minutes, phenol vapor, 2-3 hours) than in some of the heavily armored beetles. Blue green changes through green and brass yellow to copper red, yellowish green changes through brass yellow and copper red to purplish copper. On removal of the swelling agent the color passes through the above series in the reverse direction until the original hue is regained. The colors of insects treated with swelling reagents change with increasing angle of incidence, to colors preceding them in the above series.

Pressure is not easily applied in an effective manner, for the integument is highly convoluted and tends to flatten out without itself being much compressed. Any flattening means a change in the inclination of some parts of the surface and a consequent change of color which is not a pressure effect at all. This source of error may be avoided if a small flat fragment of integument is chosen for study and if attention is directed only to portions of this which are not suffering a change of curvature but only a change of thickness. With these precautions, the color change observed may be ascribed to pressure, particularly since the recovery of the original hue is relatively slow when the pressure is slackened, and the points of greatest pressure show a distinct alteration of hue however they may be inclined. All this may be followed under the vertical illuminator. The colors change in the same manner as with increasing angle of incidence, passing through green and blue to violet. As the tissue recovers the colors change in the reverse sequence.[2]

Immersion in liquids of various indices of refraction does not have as pronounced an effect as in the case of the iridescent scales. This is due pri-

[1] Wood: "Physical Optics," 167 (1911).

[2] Onslow criticizes Mallock's statement as to the effect of pressure on the color of iridescent integuments, on account of being unable to duplicate his observations. The present writer has had no particular difficulty in demonstrating the color change under the microscope. It is possible that Onslow's method (pressure under the surface of a convex lens) did not permit microscopic observation, for the changes might be missed by the naked eye.

marily to the fact that the integument is not readily penetrated and possesses no internal air spaces. However, there is a distinct loss in brilliancy when the liquid is brought into contact with the outer surface, and the color may change from swelling.

The foregoing description of the optical properties of *Lytta vesicatoria* applies equally well to a number of other beetles. *Cicindela sexgutta* (*Cicindelidae*) has a very similar convoluted surface, with polygonal cuticular areas; color range and response to various tests are parallel. Other iridescent species of *Cicindela* behave similarly.

Other varieties of *Lytta vesicatoria* resemble the above very closely in optical properties, but are of particular interest because they may illustrate an exception to the rule that many writers have tried to establish, regarding the color change with increasing incidence. Instead of changing toward blue or violet ("toward the longer, or most refracted, wave-lengths," as commonly stated) the deep blue-violet passes through reddish purple and copper red to brass yellow at grazing. Similarly colored specimens of *Calosoma wilcoxii* (*Carabidae*) and *Platynus cupripennis* (*Carabidae*) show the same change toward red or orange, as do some color phases of *Strongylium bicolor* (*Tenebrionidae*).

Beetles having integuments relatively free from convolutions or pitting are more slightly metallic than those just described, and show more striking color changes with changing incidence, but otherwise they exhibit the same optical properties. The *Buprestids* have been studied by a number of workers. *Thilocteanus rubroaureus* is notable for its brilliant metallic lustre, closely resembling copper. This changes to blue-green at grazing incidence; certain other parts of the insect, yellow-green at normal incidence, change to blue. On swelling, the copper becomes purple, changing to green at grazing. The effect of pressure and the polarizing properties are similar to the preceding specimens, as are the other optical features.

The most interesting evidence is furnished by scrapings from the surface face of the integument. These may be obtained by means of a very sharp scalpel, the operation being carried out under the microscope with vertical illumination so that the depth of the removal may be observed. If the blade of the scalpel does not cut, but only slides over the surface a color change may be observed which is due to compression. Actual scraping of the surface removes thin shavings without going deep enough to lay bare the black pigment in the underlying tissue; the scraped area may appear a darker red, due to this black showing through. The shavings are only 1-2μ thick and may be thinner at their edges. There is doubtful evidence of a laminated structure. They show all the optical properties observable on the integument and are obviously the seat of its iridescence. These properties are observable equally well from either surface of the shaving. Pressure causes a striking alteration in hue, from copper-red through yellow-green to blue or violet, this is probably because there is no cushion of softer tissue beneath the color-producing

layer as there is when on the insect. The transmission color of the scrapings is a very pale, slightly greenish brown. Immersion in liquid appears to cut down he lustre very little.

Tetracha carolina (*Cicindelidae*) is similar in optical properties to the beetles already described but the distribution of its coloring is noteworthy. The elytra range from purplish copper on their inner edges, through brass yellow to deep bluish green at the outer edges. With increasing incidence these color zones appear to *shift* toward the inner edges of the elytra. *Platynus cupripennis* exhibits similar color distribution and shifting with varying incidence. The abdominal segments of *Calosoma scrutator* and *C. wilcoxii* show similar properties. An even more striking specimen is *Tetraphyllus* (*Tenebrionidae*), which shows the color range in four spots on its back, the centers of these are purplish copper, and they vary through brass-yellow, green, and blue to violet at their edges, giving patches of color like oil drops on water. Other species of *Tetraphyllus* show similar coloring. *Phanaeus carnifex* (*Scarabaeidae*) also shows the shifting of color in its prothorax. Species of *Chrysochroa* furnish many excellent examples of shifting of adjacent colors.

The optical properties of foregoing insects have been discussed at some length because they illustrate certain typical featues; the following *coleoptera* are essentially similar in optical behavior to *Lytta vesicatoria*:

Cicindelidae: Cicindela sexguttata, C. limbalis, Tetracha carolina.
Carabidae: Calosoma scrutator, C. wilcoxii, Platynus cupripennis.
Buprestidae: Buprestis striata, Castalia bimaculata, Chrysochroa fulgidissima.
Scarabacidae: Dichelonyx elongata, Phanaeus carnifex.
Tenebrionidae: Strongyllium bicolor, S. violeceum, Tetraphyllus.
Chrysomelidae: Chrysocleus auratus.

A number of unidentified beetles studied also exhibit similar properties.

Of *Diptera* studied, *Dolichopus canaliculatus, Lucilia,* and other "blue bottle" flies also show typical "metallic" iridescence.

In the above specimens the color-producing layer is relatively thin, but this is not necessarily always the case. *Plusiotis gloriosa* illustrates an exceptional structure, and is worthy of detailed description, for it serves as a link between "metallic" and "enamel" iridescence.

The integument of this beetle is marked by exceedingly lustrous, pale yellowish-green longitudinal stripes, which appear almost as brightly metallic as burnished silver, particularly when seen against the matte yellow-green back ground of the rest of the surface of the elytra. The reflection from the silvery stripes is specular, and under moderate magnification it is seen that the whole integument exhibits strictly specular reflection also. Its microscopically matte portions consist of a finely "embossed" surface, all parts of which reflect strongly, but since only parts of the tiny bosses are in position to reflect with any given direction of observation and illumination, the rest of the structure appears dark. As a result the microscopic appearance is that of a darker shade and duller lustre than corresponds to the individual elements of the surface as seen under the microscope.

Both the silvery and matte green portions of the integument are very stiff and brittle, and are distinctly different from the insects described above in that the iridescence is not wholly at the surface, but comes from a relatively thick layer of tissue. This may be demonstrated by highly oblique sectioning, or by careful scraping or "shaving" of the surface. A considerable thickness of material may be removed without destroying the color and metallic lustre, and the fragments removed by this treatment are themselves equally metallic and colored as seen from either surface. If the underlying tissues are removed, the under side of the color producing layer is quite as colored and lustrous as its outer surface. The color production appears to take place throughout the layer, rather than being localized in any given stratum of it.

Scraping reveals two other points of interest. The matte portion remains matte, even when it is scraped to give a plane surface, and its "bosses" still present their original appearance, indicating that their reflecting surfaces are independent of the surface of the layer. When the scraping is carried so far as to remove most of the outer part of the color producing layer, the underlying portions of it present a golden to deep red color with undiminished metallic lustre. This indicates that there is a certain amount of pigmentation *in* the layer in addition to the pigmented tissue beneath it.

Sections of the elytron confirm the above observations. There is an outer cuticle, 1-2 μ thick and beneath it a transparent layer about 8-10 μ in thickness. A moderate amount of yellow to brownish red pigment is distributed diffusely through the under portion of the transparent layer. Beneath this lie the heavily pigmented layers and fibrous tissues which compose the elytron. The transparent layer is evidently the seat of the color production. The matte portions of the elytron show its embossed character distinctly, as rather evenly spaced elevations, and corresponding depressions on the under surface.

Between crossed nicols these embossed regions of the layer do not extinguish as a unit, as does the smooth region, but on revolution each microscopically curved portion extinguishes in a position tangent to the planes of the nicols. This indicates a curved orientation of the tissue where the bosses rise up (like the folding of geological strata).

On account of the hardness and brittleness of the color-producing layer, sectioning is difficult, but sections 1-2 μ thick show no trace of any laminated structure. However, fractures oblique to the surface give indication of very fine laminations; these are evidently so intimately fused that they do not result in any tendency toward cleavage parallel to the surface of the layer. There is no indication of any porosity in the color-producing layer, and this is borne out by the total lack of change on prolonged soaking in penetrating liquids.

The hue of *Plusiostis gloriosa* is microscopically uniform except where a "fault" (analogous to "fault bars" in feathers) occurs due to the localized imperfections of development. Such faults invariably show the same series of colors: on a normal yellow-green, blue to purple to orange to black at the

center of the fault. Slight faults may show only the first colors of this series. They occur in the silvery stripes as well as in the matte green areas.

The iridescence exhibited by *Plusiotis gloriosa* is modified by the embossed portions of the color-producing layer, so that on account of the number of minutely curved surfaces some are always in position to reflect light at any angle at which the general surface may be placed, yet this angle may be far from definitely observable, and strictly normal or grazing incidence may be almost unobtainable. As a consequence the color changes are relatively slight on the matte portions, though the general tendency is from yellow green to bluish green. The silvery stripes are relatively unsaturated in hue, and their metallic lustre predominates over their color so markedly that little change is observable here. The hue at normal incidence is yellowish silver, becoming somewhat greener at grazing. The iridescence is much more marked if the specimen is observed in benzene, which cuts down surface reflections and permits a larger angle of incidence *in the layer*.

The faults, however, exhibit very pronounced iridescence, their colors changing toward ones following them in the series given above, as the angle of incidence is increased. (This gives the appearance of the fault expanding to cover a larger area.)

By transmitted light the color-producing layer is practically colorless in thin sections normal to the surface, except for the pigmentation of its lower portion. Scrapings tangential to the surface, taken above the pigmented stratum, show distinct transmission colors, unsaturated purplish red predominating. The saturation increases with the thickness.

Pressure cannot be supplied very effectively to the surface of the elytron, but the slight change observed by reflected light is toward the blue. Fragments show this change much more distinctly, and their transmission color also changes through red-orange to yellow.

Bleaching has no effect on the metallic lustre or color, except to destroy the dark background furnished by the underlying pigmented tissue.

Swelling agents do not act readily, probably because of the thickness and impermeability of the layer: they tend to cause the green to change to brass yellow or even orange.

Maceration in acids or alkalies causes some swelling, but the tissue is attacked severely, and the lustre and color are soon destroyed. No evidence of laminations or development of permeability is revealed by this treatment.

Nature of Iridescent Coloring of "Metallic" Integuments

It is manifest from the descriptions of the various examples of "metallic" integuments that their optical properties bear a striking resemblance to those of iridescent scales, and a comparison with thin film colors seems justified. Reference to the list of properties discussed in connection with iridescent scales[1] shows that the first ten of these are shown perfectly by the metallic integuments. The specular reflection, of high intensity, with colors easily recog-

[1]Mason: J. Phys. Chem. **31**, 348 (1927).

nizable as lying on the second and lower third order of Newton's series, the polarizing properties and the predictability of color change with varying incidence, swelling, pressure, or distribution, constitute strong presumptive evidence in favor of thin films as an explanation. The eleventh point, the loss of color on penetration by liquid, is applicable only where air voids are present, and there is no evidence of these in the "metallic" integuments.[1]

The twelfth point is the basis of the most cogent evidence against the theory of selective reflection ("surface color"). Rayleigh[2] emphasizes the fact that selective reflection is always accompanied by strong selective absorption, the solid dye-stuffs are good examples of this. If any selectively reflecting substance is present in the above specimens it must be of a character utterly at variance with any now known, with no appreciable transmission color and with great resistance to bleaching agents. The susceptibility to pressure and swelling of course points strongly toward a structural basis of the color. Onslow's polishing experiments which showed a more or less sharply defined layer of contrasting color beneath the external iridescent material, may be explained on the basis of the compression of the structure or by assuming it to have different color-producing properties at different depths. The most obvious explanation, however, is simply that the lower layer of the color-producing structure is pigmented, and that its absorption color is superposed on that due to structure itself, without loss of metallic lustre. The hue of the pigment varies with concentration and thickness from straw yellow to orange to blood red to brown, so a variety of colorings are possible. In any case this is not evidence for or against the thin-film theory.[3]

The present Lord Rayleigh's paper[4] adds quantitative evidence to the qualitative reasons offered by his father regarding change of color with incidence. This is much more marked in beetles than in any known case of surface color. "Moreover, the broad central band with lateral maxima conforms exactly to the requirements of the theory of multiple reflexion from thin plates. On the other hand, so far as I know there is no absorption spectrum or surface reflexion spectrum having these features."

If thin films are thought to be the cause of the iridescence of "metallic" integumentes, some postulate as to their character is in order. Since both surfaces of the color-producing layer may be brought in contact with liquid without loss of color, multiple thin films are necessary. These need not be

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[1]Biedermann thought that *L. vesicatoria* had air spaces which were filled slowly with liquid on soaking, because the color went from green to bronze. Onslow ascribed this to a "clearing" action, the liquid rendering the elytron more translucent, and lessening the dark background. However, the swelling action of the liquid is probably the chief factor, since gaseous swelling agents can produce the same color change.

[2]Phil. Mag., (6) **37**, 98 (1919).

[3]Onslow, after comparing the appearance of some of his "polished" specimens with that of oxidized copper, cites Mallock's paper (Proc. Roy. Soc., **94 A**, 561 (1919)) as evidence against the latter showing thin-film colors. Evans (Proc. Roy. Soc., **107 A**, 228 (1925)) and Mason (J. Phys. Chem., **28**, 1233 (1924)) have come to the conclusion that the oxide colors are due to thin films.

[4]Proc. Roy. Soc., **103 A**, 233 (1923).

many in number, for a single one has lustre and reflection color nearly intense enough, as Onslow admits on the basis of his quantitative comparisons. Moreover, the transmission color, apart from pigment, is too faint for more than a very few films to be present, unless these are separated by a medium of nearly their own refractive index.

Probably the situation is like that existing in iridescent wing membranes,[1] with several (say three or more, depending on the space available) thin films, substantially uniform in thickness and parallel, enclosed and welded together by material having a different index of refraction than their own.[2] Such a system is capable of showing all the properties exhibited by the "metallic" integuments, and furnishes the simplest explanation of them. The gradual variations in hue correspond to gradual changes in thickness of the films, while the striking local variations seen under the microscope are as easily explained. "Faults," where the structure is stunted due to hindrance during growth, always are colored to correspond to thinner films. The possibility of several different color phases of a given species is to be expected, since growth conditions or other factors may vary the development of the color-producing structure enough for this to be noticeable.[3]

The effect of dark pigment beneath the color-producing structure would be to enhance its lustre and brilliancy, just as in the case of other thin films. On the other hand, if this structure is itself heavily pigmented the coloring and lustre may be cut down; this might explain why some of the beetles, *Carabus auratus* for instance, are hardly as brilliant as a single thin film. The pale iridescent colorings of freshly hatched beetles and the development of greater brilliancy with age may be explained on the basis of increased pigmentation of a neutral hue.

The changes of hue noted in old museum specimens[4] would correspond to a thinning of the films as they aged.

The various cases of color change soon after death, though not investigated by the writer, may well come under a similar explanation, while permanent destruction of the color may be due to irreversible shrinkage or coagulation of some of the more hydrated material of the color-producing system. Ob-

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[1] J. Phys. Chem., **31**, 322 (1927).

[2] The thickness required is not inconsistent with that available, since the epidermis of most of the specimens is something over 1μ in thickness. *Plusiotis gloriosa* affords space for 50 or more laminae in the thick color-producing layer of its integument.

[3] Several specimens of *Strongylium bicolor* ranged from metallic yellowish green to purple. Similar color variation was noted in the case of *Lytta vesicatoria*, and the *Cicindelidae*, and indeed it is to be expected where ever a number of specimens are available for comparison. It might be of interest for the entomologist to correlate this with the age or conditions of development of the insect.

[4] Beddard: Animal Coloration (1892) says of a twenty-five year old collection: "Beetles whose natural color was a brilliant red had not diminished in brilliancy but had changed to green, pale yellow [pigment] had deepened into brown, blue into black, while the green color of some had been converted into purple." Each of these changes, with the exception of the pigment, is what would be expected if the color-producing films become thinner.

viously the alteration of the structure need not be very great to bring about the loss of its iridescence.[1]

The thin-film theory enables one to explain the peculiar behavior of *Buprestis*, near *trisulcatus*, which is apparently black at vertical incidence, changing to metallic red at grazing. Immersed in benzene, the color changes through this red to brass yellow and finally to blue green. Under the microscope it is seen that the areas which appear black to the naked eye are actually a deep purplish blue. The green stripes and spots on the elytra, and the similar coloring of the abdomen behave as typical cases of metallic iridescence. The dark areas are covered with epidermal scales, heavily pigmented, but these are almost completely suppressed in the metallic portions of the integument.

The color changes exhibited, particularly the whole series in benzene, locate the color at normal incidence as the blue of the lower third order in Newton's series. This is a color of very low brilliancy in metallic insects and in iridescent feathers, and may be almost black when originating in heavily pigmented tissue. At larger angles, where the color changes to one of greater brilliancy, the pigment cannot supress it so completely, and the red becomes clearly apparent. This is further accentuated by the increase of reflecting power of the color-producing structure with increasing incidence. That the pigment does serve to mask the coloring may be shown by careful scraping to remove the epidermal scales. The underlying color-producing structure is revealed, and is much more metallic and brilliant. Bleaching affords another means of eliminating the effect of the pigment, and permitting the full color to be observed.

The unique structural character of the color-producing layer of *Plusiotis gloriosa* is related to its unusual optical properties. The presence of practically resolvable laminations extending through such a thick layer constitutes a system of many more films than in the ordinary metallic integument. Such a number is not necessary for brilliance of coloring in an air-chitin system, but where the layer is "solid" and almost optically homogeneous, the saturation of the colors, particularly by transmitted light, is seriously diminished unless a considerable number of laminae function. This explains why the transmission colors in *P. gloriosa* are so much more evident than in other metallic integuments. The transmission colors are distinct enough so that their changes with pressure can be followed just as in the case of butterfly scales of the *Urania* type. The sequence of colors is seen to be that corresponding to thinning the films.

The lack of marked difference betweeen the refractive indices of the laminated layer renders hopeless any attempt to resolve the multiple film structure

[1]Liesegang (Kolloid. Z., 7, 308) states that turbid $BaSO_4$ or AgCl suspensions in gelatine become transparent on drying, due to the increase in refractive index of the surrounding medium. A similar evaporation might be sufficient to render the multiple-film sytsem optically homogeneous, and unless the hydration were perfectly reversible the color would not be restored on moistening. Similarly, reagents which destroy the iridescence (NaOH, HNO_3, etc.) may act to change the refractive indices of the films and to render them more nearly alike.

in sections, for the limit of resolution of the microscope (*ca* 0.2.μ) can only be approached with "contrasty" preparations. With objects which are almost optically homogeneous, structures three times as coarse as this may be unresolvable. The only histological evidence of the laminated structure is given by obliquely fractured surfaces, and even here the whole layer is so coherent that there is hardly any tendency for the fracture to occur along the laminae the way it does in the air-chitin lamellar structure of iridescent scales.

The silvery stripes of *P. gloriosa* do not show as marked color change with angle as is common on smooth metallic integuments. This is due to the fact that its reflection color (2nd order greenish yellow) is not as sensitive to changing angle as are either green or red iridescent colors. It is also probable that the uniformity of the laminae is less perfect in the stripes, thus decreasing the purity of the color and its changes, without diminishing the metallic lustre which is so striking. At the edges of the faults in the silvery stripes the colors (of the lower orders) show typical iridescence in accordance with the thin-film theory. It may be that the thinned laminae are more uniform here also.

The thin-film theory of the iridescence of metallic integuments has been widely held by workers in the field of structural color, but Michelson's conclusions in favor of selective reflection ("surface color") apparently caused some misgivings, and even Onslow appears to incline toward this latter theory. It need only be repeated here[1] that we know of no selectively reflecting material which does not absorb light very strongly and show an intense color even in very thin layers. The brilliant color and lustre of specimens bleached to a pale straw color by transmitted light is utterly at variance with the properties of substances which exhibit selective reflection. The effects of swelling and pressure, the amount of color change with angle, and the distribution of hues present are also thoroughly inconsistent with the known properties of these substances. Michelson's quantitative physical studies are opposed by other quantitative studies by Rayleigh and by Merritt, the latter workers having used for comparison specimens known to consist of thin films. Michelson did not take this precaution, and there is reason to believe that the curves which he obtained might also be obtained from specimens of single or multiple films, as well as from the various feathers and insects which he considered to owe their iridescence to selective reflection. It is unfortunate that an indirect study of such doubtful positive character should have been the basis of a conclusion which ignores the multitude of independent investigations and easily verifiable properties thoroughly inconsistent with it.

Biedermann considers thin films to be the cause of metallic iridescent coloring, but puts most emphasis on another type of iridescence, which he characterizes as *"émail."*

[1]The objections to the "surface color" theory have been discussed in detail in Part II of the present series of articles, and in Part II of that on insect colors.

"Enameled" Iridescent Integuments

The type of iridescence which Biedermann compared to enamel is distinctly different in appearance from the metallic iridescence just described, though its optical nature is closely related, particularly to the structure possessed by *Plusiotis gloriosa*. The characteristic feature of "enameled" iridescence is its satiny matte lustre and its apparent "depth." Specular reflection is absent and the color appears to be scattered from beneath the surface of the integument. A peculiar shifting luminous shadow is also noticeable. Cetonids of several genera offer good examples, and this group seems to be the only one in which this type of iridescence is at all common.

Euphoria fulgida is typical of a number of *Euphorias* as well as of the "enameled" beetles in general. Structurally it is rather similar to *Plusiotis gloriosa*. The integument possesses a color-producing layer 20 μ or more in thickness, all levels of which give rise to the color. Surface examination and tangential or oblique sections reveal a finely stippled or dotted appearance in this layer. The "dots" are very minute (say 0.3 μ in diameter) and are less than 1 μ from center to center, unsystematically arranged but uniformly distributed. Sections normal to the surface show that these dots are the ends of fine rods extending through the color-producing layer, in general perpendicular to its surface, but occasionally slightly tilted. No other periodic structure is evident; fractures oblique to the surface give little if any indication of laminations. The surface of the cuticle exhibits a thin outer layer (1-2 μ) divided into polygonal areas. This may be removed without affecting the iridescence. Sections of the enamel layer are anisotropic and between crossed nicols the rod structure shows up plainly. *E. fulgida* is very lightly pigmented as compared with the other "enameled" beetles, the elytra being a dark straw color by transmitted light. Painting the under surface of the elytra with india ink cuts down the effect of the transparent underlying tissues, and serves as a dark background to enhance the iridescent coloring very markedly.

The color of the enamel layer is a slightly yellowish green by reflected light (some specimens range from green to blue), pale straw (pigment) by transmitted light. Although the brightness is greatest in the vicinity of the angle of the reflected ray, light is scattered also, and the color may be observed over a considerable angle with unidirectional illumination. The intensity of reflection is high, and the specimen under favorable light may appear almost self luminous. "Faults" in the color-producing layer are blue green to purple. Apart from these the color is uniform. With large angles of incidence the reflection color is blue green. This is best observed when the specimen is immersed in benzene so as to eliminate surface reflections which decrease the saturation of the color as grazing incidence is approached. Such procedure also insures that the angle of the incident light in the color-producing layer shall not be limited by the critical angle of chitin. The "faults" change from blue-green through purple to dark at grazing. The angle of vision, rather than the angle of illumination, determines the color changes observed. The

tissue beneath the color-producing layer may be removed by dissection or by maceration in dilute HNO_3. The exposed under surface shows the same color phenomena as the outer surface. Very thin scrapings, if not completely distorted, are capable of producing the color. Sections normal to the surface do not give the iridescent color, but with unilateral dark field illumination may show non-uniform diffraction colors, as would be expected from such a periodic structure thus illuminated. The color is of full intensity in diffuse light, and is independent of the azimuth of the illumination or observation. No polarization effects were observed, except such as are manifested by any finely divided system (similar to Tyndall blue).

The luminous shadow, which is characteristic of enamel iridescence, is exhibited only at small angles of incidence, and is seen along the line of direct reflection (in the position of the high light on a smooth surface).

Swelling agents, such as NaOH, cause the green to change through brass yellow to orange red, and this change is reversed on thorough washing or neutralization of the alkali by an acid. Bleaching does not destroy the iridescence, though all the pigment coloration may be destroyed. This enables the true transmission color of the iridescent layer to be observed, and it is seen to be a pale pink. Pressure alters the color from green through blue to purple, and the transmission color (as seen in bleached specimens) changes through orange to yellow. Penetration by liquids is not possible in the untreated layer, but may be effected after maceration in HNO_3. This reagent renders the color-producing structure porous, probably by dissolving one variety of chitin, (of which the "rods" consist). The attack spreads from cracks in the layer, and the unaltered material is thus available for comparison of hue and brightness. The HNO_3 may be replaced by liquids of various refractive indices with the following changes in appearance:

Air $n = 1.00$ Whitish blue scattered; dark brown by transmitted light; pores distinct.

Water $n = 1.33$ similar to above, but less bright and opaque.

Xylene $n = 1.49$ perfect match for unaffected portion of color-producing layer.

Mixture $n = 1.58$ no color effect whatever; pores wholly invisible even with dark field illumination.

α —Monochlornaphthalene $n = 1.63$ similar to unaltered portion in hue and brightness

Methylene iodide $n = 1.74$ brighter colored and more opaque; pores more distinct.

Methylene iodide + sulphur $n = 1.78$ whitish blue replacing normal iridescent color.

Refractive index of layer 1.594 by Becke test.

The same specimen may be run through the series of liquids in any order, with the corresponding changes in appearance. The penetration or evaporation of liquid appears to take place in patches, as if the color-producing layer were composed of fairly large cells so perfectly fused together as to be invisible ordinarily.

A very brilliant Cetonid, *Sphellorrhina guttata*[1] might be described in practically the above words, except that it is more of an emerald green, and changes at grazing incidence to blue. The prominent spots consist of white scales overlying depressions in the enamel-layer, which is thinned and stunted beneath them, and colored in the same manner as if a "fault" were present. Scraping the enamel layer has no effect on the color or lustre until the inner portion is reached, when the color goes toward blue. Beneath this is a layer of dark pigment.

Heterorhina (*Coryphocera*) *decora* Ill. is the most striking of the enameled beetles, with brilliant red thorax and stripes across black elytra. These stripes appear almost as luminous as glowing coals. With increasing incidence their color changes through yellow and green to blue-green. At the edges of the red stripes their coloring is graduated through the above lines, before it meets the surrounding black-pigmented portion of the elytron. Faults, and the inner portions of the enamel layer (as revealed by scraping) show this same series of colors.

The red portions of this insect, even when thoroughly bleached, show a pale green by transmitted light, while those areas which are green exhibit a pink transmission color, as does the green of *Sphellorrhina guttata*. The effect of pressure on fragments of the red areas is noteworthy, in that the green transmission color changes to pink and then to orange, while the red reflection color passes through yellow-green and blue-green to blue.

Nature of Iridescent Coloring of "Enameled" Integuments

In spite of the marked differences in lustre, "enamel" iridescence resembles that of thin films rather consistently. The colors and their changes with angle of incidence, pressure, swelling, or "faults," the complementary character of the transmission colors, and their low saturation, the loss of color on penetration, after treatment with HNO_3, the persistence after bleaching or in diffuse light—all these criteria are fully satisfied, and they could not be met by any other known type of structural color.

The discrepancies which exist may be explained on the basis of the modification of the structure by the fine rods which perforate it perpendicular to the surface. It was first thought by the writer that these were the chief cause of the enamel iridescence, and that they acted as some sort of a point grating by virtue of their uniformly minute dimensions. This cannot be the case, since diffraction colors demand unidirectional light, while these are unimpaired even in thoroughly diffuse light. Comparison with a number of other Cetonids, not "enameled" but either metallic or non-iridescent, reveals a similar rod structure in their integuments, so there can hardly be any significant connection between it and the color production.

It is probable that the color-producing layer is essentially similar to that of *Plusiotis gloriosa*, consisting of many unresolvable laminae of chitin ($n =$

[1] This is probably closely similiar in appearance and properties to *Heterorhina africana* studied by Onslow, and *Smaragdisthes africana* studied by Biedermann.

1.59) perforated and welded together by another variety of chitin (n = 1.50-2) the dimensions being such as to give colors of the second and lower third orders.

In the untreated specimen the specular reflection from a system of multiple thin films is broken up by the rods, and light is scattered over a considerable angle. At vertical incidence the rod structure acts as a "light trap," like velvet[1] and since it constitutes a considerable portion of the area of the enamel layer, there is a lessened reflection that is manifest as the luminous shifting shadow (the *pseudopupille* of Biedermann). At larger angles of incidence the rods serve to diffuse both incident and reflected light, which may suffer many reflections before it emerges from the multiple-film structure, colored. A definite polarizing angle, and the other polarization effects characteristic of uninterrupted films are obviously impossible in such a system.

When the color-producing layer is treated with HNO_3 the less refractive variety of chitinous material is removed, and this may then be replaced by various media. With air the scattering action of the pores (rods) is so pronounced that it obscures any effect from the thin films, and only an opalescent white, almost opaque even in very thin layers, is observed. Under these conditions the layer functions as a Tyndall blue medium.[2]

Highly refractive permeating media have a similar action, and it is only when the pores are filled with a medium of refractive index fairly near that of chitin that the structure becomes transparent enough for the effect of the multiple films to be evident. This is best seen when the refractive index of the penetrating liquid lies between 1.45 and 1.65, 1.55 matching the appearance of the untreated layer perfectly. If the refractive index of the penetrating liquid is such as to render the system optically homogeneous (n = 1.59) then no color effect whatever is observable.

In the case of some of the more brilliant enameled beetles the treated layer, when filled with a liquid of high refractive index, may show a color different from its ordinary hue. This may be due to swelling and change of thickness of the color-producing films, or to the fact that the highly refractive layer is of greater effective thickness and acts as a thicker film. The original color is restored by pressure, which fits either of these explanations.

The descriptions of enameled iridescence given above check very closely with Biedermann's observations. He recognized its unique properties, and came to the conclusion that "the colors of thin plates are the chief factor, and the rod layer is important only in so far as it may give blues of a turbid medium and may increase the lustre because of its high reflecting power."[3] He compares the *pseudopupille* to that shown in the luminous tapetum in certain animal and insect eyes, and considers that it may function to give an effect analogous to rod double refraction.

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[1]Bancroft: "Applied Collid Chemistry," 242 (1926); Wood: "Physical Optics," 449 (1911).

[2]Mason: J. Phys. Chem., 27, 201 (1923). Structural Colors in Feathers, I.

[3]loc. cit. p. 1918.

As Onslow points out, Biedermann considers the rod layer of importance in cases of simple metallic iridescence, where it is entirely beneath the color-producing structure. Onslow classes enamel iridescence with effects due to scattering of light by fine particles, but his observations are rather incomplete, and he makes no postulates as to how the color might be produced by such a system.

Diffraction Iridescence

Since such positive opposition to diffraction as an explanation of iridescence has been expressed in various places in this series of papers, the writer is glad to be able to demonstrate that this is not purely prejudice, and that he can recognize diffraction colors when they really occur in nature.

Serica sericea is typical of a number of *Sericae*, all of which are dark-brown, highly convex beetles, showing a brilliant iridescence in direct sunlight and much less in ordinary light. In thoroughly diffuse light (such as on top of a building in a fog), no trace of iridescence is detectable. With light from a point source, even of low intensity, the colors are distinct and two orders may be observed. There is no color in the directly reflected light, and this absence of color in the high-lights is another good test for this type of iridescence. With light and line of vision falling lengthwise of the elytra, as the line of vision is moved away from the directly reflected ray a sequence of colors is observed. Through about 90° they are roughly as follows: blue, green, yellow, orange, red, purple, blue, green, orange, red. With light and line of vision falling across the elytra, no color effects are noted.

The above variation of iridescence with azimuth leads one to look for some oriented structure, which is found in the form of fine striae running crosswise of the elytra. These are shallow (0.5-1.0 μ), and very evenly spaced (1-1.5 μ, or about 20,000 per inch). That they are at the very surface of the cuticle may be shown by means of collodion impressions[1] which retain the same pattern. The iridescence is exhibited by these impressions quite as well as by the insect, and may also be observed by transmitted light. If the surface of the elytron is covered with liquid, the iridescence is decreased markedly and is not observable if its refractive index differs from that of chitin by less than about ± 0.1.

All the above properties are perfectly in accord with those of diffraction gratings, and there can be no question as to the striae functioning as a remarkably perfect grating, particularly since their orientation on the elytra is crosswise of the direction in which the light is diffracted. The fact that the red is deviated more than the blue is also a significant point in the identification. No such set of properties could be manifested by thin films, surface color, turbid media, or any other known color-producing structure except a grating. The high degree of convexity of the elytra enhances the effect, and renders several colors visible at one time, as a sort of "rainbow" transverse of the elytra.

[1]These impressions are made by flowing syrupy collodion (or duPont cement) over the surface, and stripping it off after it hardens.

Conclusion

It appears from the evidence discussed in the foregoing pages that thin films are the cause of nearly all types of iridescence in insect integuments, as they are also in insect scales and in feathers. Although this seems a complicated way for nature to produce the color, yet it must be borne in mind that once the possibility of a laminated structure is admitted, the hue is only a matter of thickness, while the degree of saturation and lustre are dependent on the number and uniformity of the films. The most significant property, that of hue, can thus be varied through the whole range of color by a much more simple means than by the synthesis of a variety of special pigments. Incidentally, the colors so produced are "fast" enough so that they have endured in the inlaid ornaments of Egyptian tombs.

The conclusions of this paper are as follows:

1. "Metallic" iridescent insect integuments owe their color phenomena to a thin laminated layer at or just beneath the surface, which acts as a multiple thin film.

2. The color-producing structure may be much thicker, with many more laminae, as in *Plusiotis gloriosa*, where it is embossed rather than smooth.

3. "Enameled" iridescent integuments owe their color phenomena to a thick multiple-film layer, the properties of which are modified by the closely spaced, minute rods which perforate it.

4. Diffration iridescence has been identified in *Serica*, but does not occur in "metallic" or "enameled" integuments.

5. The properties and criteria for identification of the above types of iridescence are discussed in detail.

6. Selective reflection ("surface color") is not exhibited by iridescent insect integuments.

Laboratory of Chemical Microscopy
Cornell University

THE INFLUENCE OF SALTS ON THE OPTICAL ROTATION OF GELATIN. I.*

BY D. C. CARPENTER

The first attempt to connect hydrogen ion concentration systematically with the optical rotation of gelatin appears to have been the work of Bogue and O'Connell.[1] These authors examined this relationship at 30°C. with 2% solutions of ash-free gelatin.

Shortly afterwards more detailed experiments on the relation of pH to the optical activity of gelatin were made by Kraemer[2] who examined the influence of pH and of temperature. Among other things, Kraemer showed that gelatin derived from calfskin possessed entirely different optical properties from that derived from pigskin. In the writer's laboratory the work of Kraemer has been confirmed and extended,[3] showing also that for low temperatures, time is a considerable factor in attaining optical equilibrium at any given pH value. The gelatin solutions we have examined, showed that equilibrium was not quite attained even after three days at 0.5°C. In the present work seven days has been allowed for final equilibrium of the solutions at low temperatures.

Pauli, Samec and Strauss[4] have examined the effect of a few salts on the optical rotation of horse and beef serum and egg albumin. Their results indicate that in alkaline solutions the valence of the cation of the added salt influences the rotation, while in acid solutions the valence of the anion of the added salt causes the principal effect.

In 1920, C. R. Smith[5] showed that at temperatures above 35°C. gelatin existed in one form ("sol form") and had a specific rotation around −141°, while at lower temperatures the specific rotation increased enormously. This he attributed to a bi-molecular reaction in which the "sol form" was converted into the "gel form" (at lower temperatures) which possessed a much greater levo-rotation.

Experimental Part.

For the work described below, a very high grade of gelatin, prepared from calfskin, was de-ashed at the iso-electric point (pH 4.7) by electro-dialysis and purified and dehydrated by the method described by Sheppard, Sweet and Benedict[6] and finally dried in vacuum at 60°C. A one-percent stock

*Contributed from the Chemical Laboratory of the New York Agricultural Experiment Station, Geneva, N. Y.

[1] R. H. Bogue and M. T. O'Connell: J. Am. Chem. Soc., 47, 1694-7 (1925).

[2] E. O. Kraemer: Colloid Symposium Monograph, 4, 102-21 (1926).

[3] D. C. Carpenter, A. C. Dahlberg, and J. C. Henning: In press.

[4] W. Pauli, M. Samec and M. Strauss: Biochem. Z., 59, 470-95 (1914).

[5] C. R. Smith: J. Am. Chem. Soc., 41, 135-50 (1919).

[6] S. E. Sheppard, S. S. Sweet and A. J. Benedict: J. Am. Chem. Soc., 44, 1857-66 (1922).

solution of this purified calfskin gelatin was prepared by swelling ten grams (dry weight) in water over night, warming to 60°C., for "solution" to take place, cooling to 25°C., and making the volume up to 1000 cc. in a volumetric flask.

After thorough shaking, thirty-five cc. samples of this 1% stock solution were then pipetted into a series of weighed flasks, the pH adjusted to 6.0 by the addition of 1.24 cc. N/10 KOH and sufficient water added by weight, to make exactly 50 grams of total water in each flask. To this series of solutions, weighed amounts of KCl, KBr or KI were added to give the molality of salt shown in the tables. These solutions were thoroughly shaken and poured into 200 mm. polarizing tubes. It has been found advantageous to coat each end of the polariscope tube lightly with vaseline before adjusting the cover slip and to permit a small air bubble to remain in the tube to obviate strains within the gels, which lead to erratic polariscope readings. The polariscope tubes were then placed in the constant temperature bath at 0.5°C ± 0.02°C., for the designated period of time, at which time they were removed and examined in the polariscope in the cold room at 0°–1°C. At the close of a series of readings at 0.5°C., the tubes were allowed to warm up to room temperature and were then placed in the constant-temperature bath at 40°C. for a half hour before polarizing again, at this higher temperature. A triple-field Schmidt and Häensch polariscope was used throughout.

The pH of the solutions was determined by the quinhydrone electrode, being set up as half cells after Biilmann. The comparison electrode was a standardized n/10 calomel electrode at 25°C. and junction was made with saturated KCl solution. The potential was usually steady after fifteen minutes and the pH calculated from the relation $pH = \frac{0.3614 - E,}{0.0591}$ disregarding corrections for junction potential and for any effect the high salt concentrations may have had upon the quinone-hydroquinone equilibrium within the cell.

Density determinations were made of all solutions at 25°C. in a carefully calibrated pycnometer. For the purpose of calculation in this article it is assumed that the density at 0.5°C. and at 40°C. are the same as that at 25°C. In many cases the density at 0.5°C. is not experimentally attainable by pycnometer as the solutions are gels. In any case the actual error will not be large if the above assumption is made.

The specific rotation was calculated from the equation $[a]_D = \frac{100 \cdot a}{l \cdot p \cdot d \cdot}$ where a is the angle measured, l the length of tube, p the grams of gelatin in 100 grams of solvent, and d the density of the solution.

Using Lewis and Randall's[7] data on activity coefficients for uni-univalent salts the activity of each salt at each concentration has been calculated and

[7] G. N. Lewis and M. Randall: "Thermodynamics and Free Energy of Chemical Substances," 344, 362 (1923).

the activity values compared with the observed specific rotation. These data for the salts KCl, KBr, and KI are recorded respectively in Tables I-III. The specific rotations at 0.5°C. after 7 days and at 40°C., and their relationship to activity of the added salt are shown graphically in Fig. 1. The salt concentrations are all calculated on a molality basis. The salts were carefully recrystallized and dried at 105°C before use in this work.

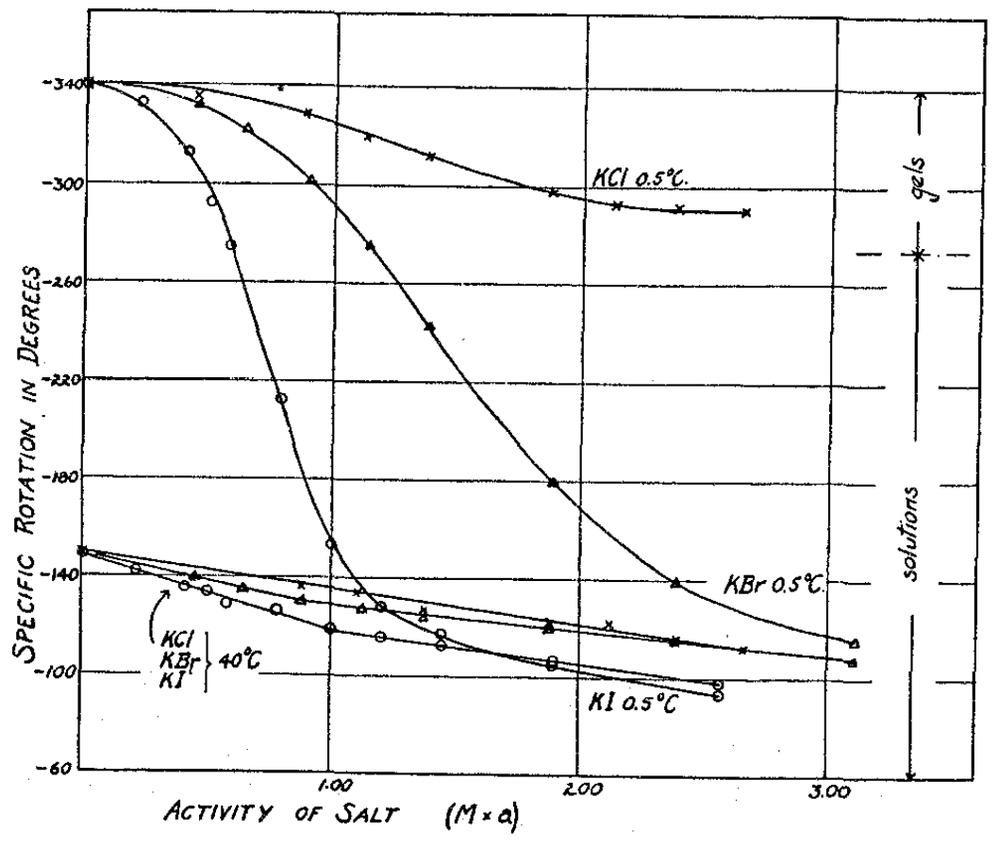


FIG. 1
Influence of Salts on the Specific Rotation of Gelatin

TABLE I
Influence of KCl on Optical Rotation of Gelatin at pH 6.0

Soln. No.	Molality of KCl Soln.	Activity Coef. (L & R)	KCl Activity (M × a)	Wt. gelatin per 100 gms. solvent. Gms.	Density at 25°C	24 hrs. $[a]_D^{0.5°C}$ levo degrees	48 hrs. $[a]_D^{0.5°C}$ levo degrees	7 days $[a]_D^{0.5°C}$ levo degrees	7 days $[a]_D^{40°C}$ levo degrees
1	0.000	1.000	0.00	0.700	0.9981	330	337	340	148
2	0.670	0.662	0.444	0.666	1.0287	326	332	335	138
3	1.341	0.654	0.876	0.636	1.0567	319	321	329	136
4	1.677	0.668	1.120	0.622	1.0698	311	316	319	134
5	2.011	0.680	1.369	0.609	1.0828	304	308	311	126
6	2.682	0.698	1.87	0.583	1.1073	287	291	299	121
7	3.018	0.704	2.12	0.571	1.1196	280	284	292	122
8	3.355	0.710	2.38	0.560	1.1313	271	279	291	115
9*	3.690	0.715	2.64	0.549	1.1423	266	277	290	112

*Solution marked with asterisk (*) pasty gel at 0.5°C.
All others were solid gels at 0.5°C.

TABLE II

Influence of KBr on the Optical Rotation of Gelatin at pH 6.0

Soln. No.	Molality of KBr Soln.	Activity Coef. (L & R)	KBr Activity (M × a)	pH 25°C	Wt. gelatin per 100 gms. solvent Gms.	Density at 25°C	24 hrs. $[a]_D^{0.5°C}$ levo degrees	48 hrs. $[a]_D^{0.5°C}$ levo degrees	7 days $[a]_D^{0.5°C}$ levo degrees	$[a]_D^{40°C}$ levo degrees
1	0.000	1.000	0.00	6.04	0.700	0.9981	331	337	341	150
2	0.672	0.662	0.445	5.92	0.6475	1.0448	323	330	332	140
3	1.008	0.635	0.640	5.92	0.625	1.0783	305	319	322	133.6
4	1.344	0.655	0.880	5.95	0.603	1.1032	284	298	302	130
5*	1.681	0.670	1.127	5.81	0.583	1.1277	260	270	273	127
6*	2.016	0.680	1.370	5.84	0.565	1.1520	224	238	242	122
7*	2.688	0.700	1.880	5.79	0.5305	1.1972	155	174	180	121
8*	3.361	0.710	2.386	6.01	0.500	1.2391	127	134	139	114.7
9*	4.200	0.724	3.110	——	0.467	1.2893	115.5	113.8	116.1	108

*Solutions marked with asterisk (*) did not gel at 0.5°C.
All others were solid gels at 0.5°C.

TABLE III

Influence of KI on Optical Rotation of Gelatin at pH 6.0

Soln. No.	Molality of KI Soln.	Activity Coef. (L & R)	KBr Activity (M × a)	pH 25°C.	Wt. gelatin per 100 gms solvent gms.	Density at 25°C.	24 hrs. $[a]_D^{0.5°C.}$ levo degrees	48 hrs. $[a]_D^{0.5°C.}$ levo degrees	7 days $[a]_D^{0.5°C.}$ levo degrees	$[a]_D^{40°C.}$ levo degrees
1	0.000	1.000	0.00	5.95	0.700	0.9981	328	336	340	148.5
2	0.301	0.716	0.215	5.86	0.666	1.0334	318	324	332	142
3	0.602	0.670	0.406	5.87	0.635	1.0668	285	298	312	135
4	0.753	0.658	0.495	5.94	0.622	1.0836	263	280	292	133
5*	0.903	0.642	0.578	5.91	0.605	1.1001	237	255	274	128
6*	1.205	0.647	0.784	6.09	0.583	1.1316	167	186	212	186
7*	1.506	0.661	0.996	6.13	0.560	1.1630	135	139	152	118
8*	1.810	0.673	1.205	6.17	0.534	1.1932	125	128	127	115
9*	2.109	0.685	1.444	6.10	0.518	1.2224	114	117	117	112
10*	2.710	0.699	1.892	6.12	0.483	1.2785	105.5	105.5	105.4	106.2
11*	3.610	0.715	2.574	6.34	0.437	1.3566	94.5	92	92.8	98.7

*Solutions marked with asterisk (*) did not gel at 0.5°C.
All others were solid gels at 0.5°C.

Discussion and Conclusions

It is to be pointed out that the above experiments have been conducted at pH 6.0, in which region we have reason to believe that the gelatin is in the form of a gelatinate salt, potassium gelantinate in the present case. According to Pauli's experiments we should expect that there would be no difference in effect by varying the anion of the potassium salt used. According to Loeb's[8] view we should also expect no difference in effect, the cation (K^+) only exerting an influence on the properties of proteins on the alkaline side of the isoelectric point and all anions being of equal or no influence.

[8] J. Loeb: "Proteins and the Theory of Colloidal Behavior" (1922).

The above experiments show conclusively that KCl, KBr, and KI each has an effect, and an effect of different magnitude on the optical activity of calf-skin gelatin at a constant pH of 6.0.

Three hypotheses as to the mechanism of this effect are possible,—

1.—That the addition of salt influences the production of the "sol form" of low optical activity at the expense of the "gel form," at a temperature where the "gel form" has hitherto been supposed to be the stable form.

2.—That the salts each form compounds with the potassium gelatinate, with a characteristic optical activity in each case.

3.—That the added salts disturb the hydrol-polyhydrol equilibrium of the solvent itself, thereby actually diluting the system and reducing the optical activity by the additon of the hydrol species which peptises gelatin, formed at the expense of other hydrol species.

In favor of the first hypothesis we may say that in all of the three cases the optical activities are very nearly alike of the solutions that have just barely passed from the gel state to the sol state at 0.5°C. This would indicate that enough of the "gel form" had been converted to the "sol form" to no longer leave sufficient of the "gel form" to produce a solid gel. At 0.5°C. and a pH of 6.0 about 0.44-0.46% gelatin is necessary to form a gel. The maximum change in specific rotation for KI is $340° - 93° = 247°$. In the KI solutions, sample 4 has barely changed from gel to sol. This has changed in specific rotation from 340° to 264°, a change of 76°. The fraction of the total change possible is $76/247$. Since the solutions contained 0.7% gelatin in the first place and $76/247$ of it has been changed, then $76/247 \times 0.70 = 0.215$ g gelatin changed. This value subtracted from the original .70 gives 0.485 a figure very comparable with 0.44 — 0.46, the amount necessary to form a gel in the absence of KI. A similar calculation for KBr gives the figure 0.465.

This effect of salts on the optical rotation, to whatever it may be ascribed, is entirely reversible, for when solutions 2, 5 and 9 of the KI series were dialysed practically free from KI through collodion membranes, the gelling property returned, and moreover the optical rotation returned to the value around −330° in each case. This does not, however, in any way show what has happened to the gelatin by adding KI. It shows only that the action is reversible and that we obtain the original gelatin after removal of the KI.

Opposed to this view we have the fact that the specific rotation of calfskin gelatin on the alkaline side of the iso-electric point at 40°C where the gel form is supposedly completely transformed to the sol form, is −148° and independent of pH between pHs 5.5 and 12. The data show, however, that the specific rotation can be reduced as low as −93° in concentrated KI solutions, a value very low to be explained simply by the sol-gel polymerization hypothesis. As practically identical values for specific rotation have been obtained at 0.5°C and 40°C for solutions of both 0.40 and 0.70% gelatin content, it can not be argued that we are dealing with the customary change of specific rotation depending on changes in concentration of the dissolved substance, in which the water content is purposely varied.

At present our very limited knowledge of the proteins, as well as the laws of concentrated solutions in general, does not enable us to approach the problem from the viewpoint of the second hypothesis with any degree of certainty.

With regard to the hydrol-polyhydrol hypothesis, it must be said that this is undoubtedly the classical explanation for certain phenomena, such as the influence of solutes on the temperature of maximum density of water. Taffel[9] has shown that the temperature of maximum density of water is influenced by both the cation and anion of the dissolved salt and it is presumably through a readjustment of the hydrol equilibrium that this takes place. It is well known that the viscosity of solutions of KCl, KBr, and KI pass through a minimum as the salt concentration increases. According to the meagre data recorded in physico-chemical tables,[10] this minimum occurs in the region of 1.0M, 2.0 M and 1.0 M respectively for KCl, KBr and KI. These data are, however, at 15° – 18°C. instead of at 0°C. At 0°C the minimum viscosity of KBr and KI solutions is recorded as around 3M. This may be attributed likewise to changes in the hydrol equilibrium by the added salt. Bancroft[11] in an article on the water equilibrium, by the process of elimination, puts forward the idea that quite probably the alteration of the hydrol equilibrium by KI is entirely responsible for the liquefaction of gelatin by that salt.

It seems possible that the decrease in optical activity of gelatin, already mentioned, below that required for the complete conversion of the "gel form" to "sol form" may be explained on the basis of a change in the hydrol equilibrium of the solvent, thereby actually producing more of the form of hydrol which peptizes gelatin and diluting the system sufficiently to account for the low value $[a]_D^{0.5°C} = -93°$ recorded.

Loeb's view of the non-influence of the anion of added salts on the properties of protein solutions held at constant pH on the alkaline side of the isoelectric point, is not in harmony with the facts here presented. The optical rotation is to be regarded as a fundamental property of the protein molecule and dependent on its structure. A change in the molecular structure of a protein may entirely change its properties as a chemical individual. On the basis of the results here reported, it would appear that Loeb's experiments[12] on the influence of salts on the viscosity of gelatin solutions should be interpreted on the "gel-sol form" equilibrium basis rather than as the direct result of the Donnan equilibrium. In any event Loeb has entirely overlooked the existence of the two forms of gelatin and their separate and individual influence on viscosity. Loeb denies the existence of the Hofmeister series at a constant pH. It is here shown that at pH 6.0 the halides of potassium form the series I > Br > Cl in their influence on the optical rotation of gelatin. Whether other monovalent anions will assume their usual place in this series, characteristic to the usual Hofmeister series, remains a matter for future investigations.

[9] A. Taffel: Trans. Faraday Soc., **19**, 99-105 (1923).
[10] Landolt-Börnstein: "Physikalisch-Chemische Tabellen," 158-9 (1923).
[11] W. D. Bancroft: J. Phys. Chem., **30**, 1194-1201 (1926).
[12] J. Loeb: loc. cit., p. 100.

It is an established fact that at no possible concentration of the halide salts of potassium can gelatin be precipitated from solution. This is believed to be due to the transformation of gelatin to the "sol form." It is further known that gelatin is precipitated from solution as a gel, by half saturated ammonium sulfate. Sörensen[13] has shown that the osmotic pressure of egg albumin is materially decreased with increasing concentrations of $(NH_4)_2$ SO_4. This may well be due to polymerization of the protein molecule to a form comparable with the "gel form" of gelatin, as the $(NH_4)_2$ SO_4 content is increased. Svedberg and Nichols[14] have shown that egg albumin, freed from salts by electro-dialysis, has a molecular weight of 34,000, while that purified by ordinary dialysis contains a substance of molecular weight 170,000 to an extent of about 6%. Whether this material of high molecular weight was a foreign protein or was present as a polymerized egg albumin through the influence of $(NH_4)_2SO_4$ not removed by dialysis, these authors were unable to decide.

If the foregoing hypothesis is well founded, that the chief influence of neutral salts on proteins is one of polymerization of the protein molecule, such as we probably have in the case of the "gel" and "sol" forms of gelatin, we would deduce that while the halides of potassium influence the change in the direction of the "sol form," other salts such as sulfates, oxalates, etc., may presumably be expected to have the opposite effect, namely conversion of the "sol" to "gel form." Experiments are in progress to ascertain whether this actually takes place. If so, we should be able to show the direction of the change, as well as its magnitude through polariscopic examination of the protein solutions.

Summary

1.—The influence of solutions of KCl, KBr, and KI on the optical rotation of 0.7% potassium gelatinate (calfskin) solutions at a constant pH of 6.0 has been examined.

2.—Each salt produces a characteristic lowering of the optical activity, KI producing the greatest lowering, KCl the least lowering and KBr of intermediate effect.

3.—The change in optical activity is discussed and is considered attributable to the tautomeric equilibrium between the "gel" and "sol" forms of gelatin, coupled with changes in the hydrol equilibrium of the solvent produced by the added halide salt.

[13] S. P. L. Sörensen: Medel. Carlsberg Lab. Copenhagen, **12**, 255 (1917).
[14] T. Svedberg and J. B. Nichols: J. Am. Chem. Soc., **48**, 3081-92 (1926).

MUTAROTATION III. GLUCOSE EQUILIBRIA IN METHYL ALCOHOL AND MIXTURES OF METHYL ALCOHOL AND WATER

BY JOHN CLARK ANDREWS AND FREDERICK PALLISER WORLEY

Observations by various investigators of the optical rotation of glucose in aqueous solution after the attainment of equilibrium have shown that, unless an appreciable amount of a third form be present, the amounts of α glucose and β glucose present at equilibrium are in the ratio of about 37 to 63 in dilute solution. Little work has been done on the equilibrium in other solvents. Baker, Ingold, and Thorpe,[1] found in methyl alcohol an equilibrium rotation of $[\alpha]_D^{44.8^\circ} = 64.1$. This would correspond in the absence of a third form to a ratio of about 45 of α glucose to 55 of β glucose, which differs materially from the equilibrium in water. It is difficult, however, to account for the process of mutarotation without the formation of an intermediate form of glucose. Mechanisms of the process involving such intermediate forms have been advanced by E. F. Armstrong[2] and by Lowry.[3] Baker, Ingold and Thorpe on the other hand, regard the process as occurring without the formation of an intermediate compound.

If an intermediate substance is formed in the process of mutarotation, it should be present at equilibrium. Its amount would depend on the relation between the rate of conversion of the intermediate form into α and β glucose and the rate of conversion of these into the intermediate form, and would be negligibly small only if the conversion of the intermediate form into α and β glucose were very rapid in comparison with the reverse changes. Experiments carried out by Roux[4] and later by Rüber[5], which should have revealed the presence of any appreciable amounts of a third substance at equilibrium in aqueous solutions had negative results. Roux showed that if the proportions of α and β glucose at equilibrium be calculated from the optical rotation on the assumption that these alone are present, and a mixture of dry α and β glucose in these proportions be dissolved in the required amount of water, the equilibrium rotation is immediately attained. Rüber carried out more exhaustive determinations of a similar nature, employing in addition to the optical method used by Roux, methods depending on the densities and refractivities of the solutions. He found that there was no detectable change in the physical properties of the solution after dissolving the mixture of α and β glucose, calculated on the assumption that these alone were present at equilibrium. He concluded that no detectable amount

[1] J. Chem. Soc., **125**, 268 (1924).
[2] J. Chem. Soc., **83**, 1309 (1903).
[3] J. Chem. Soc., **83**, 1316 (1903); **127**, 1371 (1925).
[4] Ann. Chim. Phys., (7) **30**, 427-432 (1903).
[5] Ber., **56**, 2185 (1923).

of a third substance was present, but did not exclude the possibility of a small amount of such substance, indetectable by means of the physical methods used, being present at equilibrium.

In the hope of detecting the presence of an intermediate form of glucose at equilibrium, we have determined optical rotation at equilibrium in methyl alcohol and mixtures of methyl alcohol and water, and have made experiments similar to those first carried out by Roux, but using methyl alcohol as solvent,

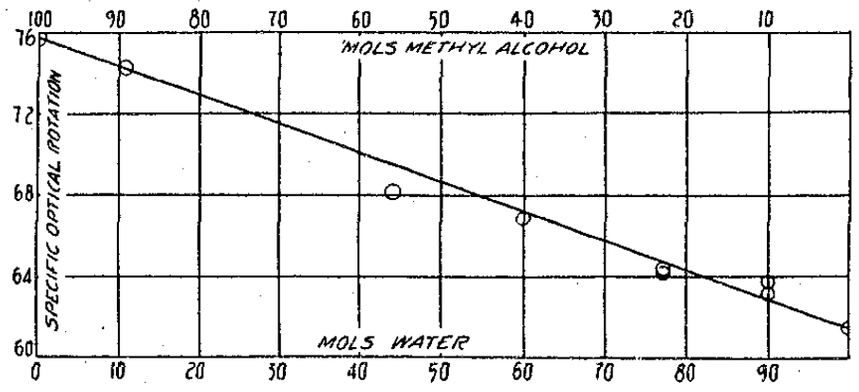


FIG. 1

to ascertain whether any detectable change in rotatory power occurs after dissolving α and β glucose in methyl alcohol in the proportion calculated to be present at equilibrium on the assumption that no third form is present. We have also carried out similar experiments in aqueous solution confirming the results obtained by Roux and Rüber.

In determining the optical specific rotation of glucose in methyl alcohol and mixtures containing only small amounts of water, the attainment of equilibrium was accelerated by the addition of traces of gaseous ammonia. The final rotation was, in general, observed about 24 hours after mixing. In two experiments observations were continued for a further seven days in order to ascertain whether any further change could be observed, but no alteration of the rotation occurred after the first 24 hours. The concentration of the glucose was from 1 to 1.5 mols. per 1000 mols. of solvent in each experiment.

The results are given in Table I and are shown graphically in Fig. 1 in which the values $[\alpha]^{25°}_{5461}$ are plotted against the molecular concentration of water and methyl alcohol, the curve obtained being a straight line.

TABLE I

Composition of Solvent

Mols Water	Mols methyl Alcohol	$[\alpha]^{25°}_{5461}$
100	0	61.5
90	10	63.8
90	10	63.2
77.2	22.8	64.4
77.2	22.8	64.2
59.9	40.1	66.9
44.2	55.8	68.2
11.0	89.0	74.3
0	100	75.8

Several experiments were carried out to ascertain the rate of adjustment of the equilibrium when methyl alcohol was added to an aqueous solution of glucose after equilibrium was attained and when water was added to a methyl alcohol solution at equilibrium. In all cases the rotation changed very slowly and finally attained a value corresponding to the proportions of methyl alcohol and water present.

The optical rotations $[\alpha]^{25°}_{5461}$ of α glucose and β glucose are respectively 129.0 and 23.8 in water and 138.4 and 26.0 in methyl alcohol. It is clear from the experimental results that as methyl alcohol is substituted for water, the equilibrium rotation gradually alters in such a way as to become more nearly a mean of the rotations of α glucose and β glucose. On the assumption that only α and β glucose are present, the results, would correspond to the presence at equilibrium of 44.3 percent of α glucose in methyl alcohol and 35.8 percent in aqueous solution, the methyl alcohol in comparison, with water, thus favoring the formation of α glucose.

It is possible that the absence of change of rotatory power observed by Roux and Rüber after dissolving the mixed sugars in water may have been due not to the absence of an appreciable amount of a third substance, but to the rotation of such substance being about the same as that of the α and β glucose contributing to its formation. It is highly improbable that this could occur also in methyl alcohol in which the equilibrium rotation is considerably different from that in water.

The results of the experiments in the case both of water and of methyl alcohol were negative, there being no detectable change in optical rotation after dissolving the sugar. The final reading in the case of methyl alcohol was taken twenty-four hours after adding a trace of gaseous ammonia.

The results of two typical experiments using water and methyl alcohol respectively are given in Table II.

TABLE II

Water 1000 mols: Glucose 35.8%	Glucose 2.0 mols Glucose 64.2%	Methyl Alcohol 1000 mols. α Glucose 44.3%	Glucose 1.67 mols. β Glucose 55.7%
Time after mixing	$[\alpha]^{25°}_{5461}$	Time after mixing	$[\alpha]^{25°}_{5461}$
5 mins.	61.4	30 mins.	75.9
1 hr. "	61.5	1 hr. "	75.8
2 " "	61.4	2 " "	75.8
6 " "	61.4	3 " "	75.9
∞	61.4	6 " "	75.7
		∞	75.8

Although these results fail to disclose the presence at equilibrium of a third or intermediate substance and although the velocity of mutarotation and the equality of the velocity coefficients of mutarotation of α glucose and β glucose under similar conditions are in agreement with the requirements of a simple equilibrium between α and β glucose, it cannot be concluded that mutarotation therefore proceeds without the formation of an intermediate

compound.[1] If the velocity of transformation of α and β glucose into an intermediate form were very slow in comparison with the reverse changes, the amount of the intermediate form present during mutarotation and at equilibrium would be exceedingly small and probably escape detection. Its formation would not appreciably affect the velocity coefficients arrived at, except at the very beginning of mutarotation.

We are investigating the initial stages of mutarotation of glucose and other sugars.

Summary

1. The optical rotation of glucose after the attainment of equilibrium in methyl alcohol and mixtures of methyl alcohol and water in varying proportions has been determined.

2. The proportions of α glucose and β glucose present at equilibrium have been calculated on the assumption that no intermediate form of glucose is present. The proportion of α glucose is increased as water is replaced by methyl alcohol.

3. There is no detectable change in optical rotation after dissolving in methyl alcohol or in water mixtures of α and β glucose in proportions calculated to be present at equilibrium in these solvents.

4. Although no intermediate substance has been detected at equilibrium and although the velocity of mutarotation of α and β glucose is in agreement with the requirements of simple equilibrium between α and β glucose, the experimental results are not regarded as eliminating the possibility of an intermediate substance being prodcued in the process of mutarotation.

We have to acknowledge our indebtedness to the Royal Society for a grant to one of us (F. P. W.) towards the cost of polarimetric apparatus and to the Duffus Lubecki Scholarship Fund which enabled one of us (J. C. A.) to take part in this investigation.

Auckland University College,
University of New Zealand,
July 8, 1927.

[1] See also Rüber: loc. cit.

THE PARTIAL VAPOUR PRESSURES OF BENZENE-TOLUENE AND BENZENE-ETHYLBENZENE MIXTURES

BY THOMAS BELL AND ROBERT WRIGHT

The deviation of the properties of a binary liquid mixture from those calculated from its composition may in general be attributed either to the breaking down of association in one or both of its constituents, or to the formation of complexes between them. It follows therefore that the more closely the constituents of a binary mixture resemble each other the greater will be the probability of the mixture rule being followed: since the more similar the constituents the smaller the chance of reaction between them.

The determination of the partial pressures of a binary liquid mixture necessitates the analysis of the mixed vapour, a process which becomes difficult when the constituents resemble one another closely. The chemical analysis of a benzene-toluene or a benzene-ethylbenzene mixture is practically impossible, and the usual physical methods of analysis by means of density or refractive index cannot be applied as the values of these constants for all three substances lie very close to each other.

In the present investigation the benzene-toluene and benzene-ethylbenzene mixtures were analyzed by adding them to a known excess of pure benzene and noting the depression in the freezing point, and from the depression produced the weight of toluene or ethylbenzene in the mixture could be calculated. As a preliminary, the effect of toluene and ethylbenzene on the freezing point of benzene was determined for concentrations of solute up to about 5%. The results are given in Tables I and II and from the almost linear curve obtained the composition of a mixture of known freezing point.

TABLE I

Depression of F. Pt. of 100 g benzene by addition of toluene.

Weight of toluene	Depression of F. Pt.
0.778	0.415
1.046	0.550
1.320	0.685
1.635	0.829
1.959	0.958
2.229	1.085
2.496	1.210
2.788	1.375
3.098	1.505
3.390	1.637
4.244	2.085

TABLE II

Depression of F. Pt. of 100g benzene by addition of ethylbenzene

Weight of ethylbenzene	Depression of F. Pt.
0.350	0.170
0.630	0.313
0.983	0.475
1.176	0.563
1.343	0.650
1.767	0.840
1.190	0.895
2.325	1.100
2.607	1.223
2.899	1.360
3.198	1.503

can be found. The determinations of the partial pressures were carried out by the air-current method. Weighed bulbs, containing the pure liquid or the mixture, were placed in a thermostat at 20° and purified air led through them at a rate of about one litre per hour. The saturated air was then passed into a test tube cooled in liquid air, where the hydrocarbons were frozen and their vapour pressures reduced to zero. The exit from the cooled test tube was connected with an aspirator fitted with a manometer. The temperature of the aspirator, the barometric pressure and the manometer reading being known the volume of air aspirated was reduced to N. T. P. The total weight of the hydrocarbon vapours in the saturated air was obtained from the loss of weight of the bulbs and checked by direct weighing of the cooled test tube, the latter weight being always used in the calculation of the composition. The whole of the condensed liquid was added to a known quantity of benzene and the depression of the freezing point determined. The amount of toluene (or ethylbenzene) present can now be calculated, the benzene in the condensed vapours being determined by difference. A more correct result may be obtained by a recalculation in which the weight of benzene in the condensed vapour is added to the weighed quantity used as solvent.

The weight of each hydrocarbon divided by its molecular weight and multiplied by 22400 gives the volume of its vapour in cc under standard conditions. The partial pressures can now be readily calculated:

$$\frac{V'}{V' + V'' + V} = \frac{P'}{\text{Total pressure}}$$

where V′ and V″ are the volumes of benzene and toluene (or ethylbenzene) vapour, and V is the volume of air all under standard conditions of temperature and pressure. P′ is the partial pressure due to the benzene and the total pressure is that in the last solution bulb, i. e. the barometric height less the manometer reading. A similar calculation gves the value of P″ the partial pressure of the toluene or ethylbenzene.

The results obtained are given in Tables III and IV. The calculated values are made on the assumption that the mixture rule holds when partial pressures

TABLE III

Partial vapour pressures of benzene-toluene mixtures at 20°

Molecular % Benzene	Molecular % Toluene	V.P. found	benzene calculated	V.P. found	toluene calculated
100.0	0	74.8		0	
100.0	0	74.6		0	
67.0	33.0	48.5	50.0	8.5	7.3
54.7	45.3	40.5	40.7	10.8	10.1
43.4	56.7	34.5	32.4	12.2	12.6
22.7	77.3	18.4	17.0	17.4	17.4
0	100.0	0		22.0	
0	100.0	0		22.6	

TABLE IV

Partial vapour pressures of benzene-ethylbenzene mixtures at 20°

Molecular % Benzene	Molecular % Ethylbenzene	V.P. found	benzene calculated	V.P. found	ethylbenzene calculated
100.0	0	74.8		0	
100.0	0	74.6		0	
57.3	42.7	43.0	42.8	3.3	3.2
26.9	73.1	21.1	20.1	5.1	5.4
13.3	86.7	9.7	9.8	6.5	6.4
0	100.0	0		7.5	
0	100.0	0		7.3	

are taken as proportional to the molecular composition of the mixture. The experimental results will be seen to be in fair agreement with the theoretical, so that if complex formation takes place in the mixtures considered it must do so to a very slight extent.

Physical Chemical Laboratory,
Glasgow University,
October 3, 1927

NEW BOOKS

Cours de Chimie inorganique. *By Fréd. Swarts. Fourth edition, revised and increased. 24 × 16 cm; pp. 786. Bruxelles: Maurice Lambertin, 1926.* Many of us use Swarts' book as a means for finding out whether a graduate student has a reading knowledge of French in addition to its legitimate use as a reference book. The subject is presented under the following heads: introduction; molecular theory; metalloids; halogens; solutions; the sulphur group; the nitrogen group; the carbon group; thermochemistry; periodic classification of the elements; metals; alkali metals; electrochemistry; the copper family; alkaline earth metals; radio-activity; the magnesium family; trivalent metals; tetravalent metals; pentavalent metals; hexavalent metals; heptavalent metals; metals of the ninth group; metal-ammonia compounds; the platinum group.

There are a lot of interesting things in the book, with some of which the reviewer agrees and with others of which he disagrees. On p. 23 the author defines an element as a substance which cannot be decomposed by any methods which we can control. On p. 515 he says that the discovery of isotopes does not affect the definition of an element as given. Two isotopes form a single element. In other words, substances with the same atomic number are identical chemically.

On p. 516 the author says that "it is not possible to give a rigorous definition for a metal because there is no sharp dividing line between metals and metalloids. It is more accurate to speak of a metallic function, characterized by certain physical and chemical properties, a function more or less accentuated in all the simple substances. The essential properties of a metallic function are first to conduct electricity without transport of ponderable matter and to have a negative thermal coefficient of electrical conductance. The electrical resistance of metals decreases rapidly at low temperatures and seems to become zero at the absolute zero. At the lowest temperature which has yet been reached (+1.5° abs.) the electrical resistance of gold is zero and that of solid mercury is one ten-millionth of the value at room temperature (Kamerlingh Onnes). While carbon is also a conductor of the first class, the electrical conductance increases with rising temperature; the thermal coefficient for the electrical conductance is positive for carbon and also for boron.

"A second characteristic of elements with a metallic function—and one which was thought to be general—is that of being insoluble in all non-metallic solvents. While the metalloids are soluble in certain solvents (water, alcohol, carbon bisulphide, etc.), metals dissolve only in other melted metals. This refers of course only to physical solubility, where there is no change in the physical nature of the substance. In the last years there have been prepared colloidal aqueous solutions of a large number of metals (gold, silver, platinum, etc); but we know that these are not true solutions. But it seems to have been proved that the alkali metals are soluble physically in liquid ammonia, so that the metallic character does not necessarily connote insolubility of the element in non-metallic solvents.

"The cryoscopy of solutions of metals in molten metals, and also the determination of the vapor densities of the volatile metals have proved that the molecules of the metals are almost always monatomic. It has been suggested that this could be taken as a standard; but the noble gases are monatomic and are not metals, while some of the metals are polyatomic in solution. The best criterion of a metal is the basic property of its hydroxide. An element is a metal when its hydroxide forms hydroxyl ions."

On p. 406 there is a discussion of the carbon cycle. "The first plants, in their process of synthetic assimilation, took up water and carbon dioxide from which to form their tissues and especially the carbohydrates, such as cellulose, starch, etc., and set free oxygen. When the concentration of this latter was sufficient, animal life became possible. Nevertheless plants do not cause the total disappearance of carbon dioxide which they have absorbed during their life. After their death, destruction of the organic matter by putrefaction or fossilization brings back into the atmosphere as carbon dioxide nearly all the carbon; only the smallest fraction changes to peat, oil, or pure carbon. . . .

"The disintegration of the silicates is another cause of the disappearance of carbon dioxide. The silicated rocks, and especially the feldspars, are attacked in the course of ages by carbon dioxide. The feldspars, silicates of aluminum and of alkali metals or alkaline earth metals, and the magnesian silicates are changed to the soluble acid carbonates of potassium, sodium, calcium, or magnesium, while the alumina remains as clay, a basic aluminum silicate. The soluble carbonates are carried off by the waters and pass eventually into the ocean, where the calcium carbonate is used by the marine animals in making their shells and becomes, after the death of the organism, a sedimentary deposit, which has attained in certain places a thickness of several hundred meters, representing more than three thousand times the weight of the carbon dioxide now in the atmosphere.

"The carbon dioxide would have disappeared from the atmosphere a long time ago, had it not been for the volcanoes which are continually sending out enormous quantities of it. In addition, the rapid burning of combustibles and the physiological oxidation of organic substances add to the atmosphere, annually, large amounts of carbon dioxide, formed at the expense of the oxygen of the air."

Monomolecular hydrofluoric acid should boil at −200°; hydrofluoric acid does boil at +19°, p. 182. In the formation of the fluosilicic acid the hydrofluoric acid does not react in its capacity as an acid because no other acid behaves in a similar way. The reaction is due to the enormous affinity of fluorine for silicon, p. 137. The author considers, p. 421, that the six fluorines in fluosilicic acid are symmetrical which he takes to mean that we have a fractional valence. If the premise be granted, one must either do that or give silicon a valence of eight.

"The possibility of forming solid solutions is a better criterion of isomorphism than similarity in crystalline form. Certain substances can form solid solutions without having the same crystalline form. Sodium chlorate and silver chlorate are cases in point. The first belongs to the cubic system and the second to the tetragonal system. We account for the formation of solid solutions in such cases by assuming that substances, which are actually isomorphous in spite of having different crystalline forms, can each crystallize in both forms. Thus sodium chlorate might crystallize in the tetragonal system. Usually one of the two forms is too instable to be isolated pure and occurs only in the solid solution in which it is constrained to appear by the crystallization of the other salt. In some cases, such as potassium nitrate, the two forms can be obtained pure. This particular form of isomorphism is called isodimorphism," p. 288.

The author considers that the oxidizing action of sulphuric acid is not due to sulphate ion, p. 264; but to undissociated sulphuric acid or to its decomposition into sulphur trioxide. If this is correct, as it seems to be, we don't have one hundred percent dissociation over the whole range for sulphuric acid. The reviewer wonders whether it might not be possible to show that some cases of reduction of nitric acid or nitrates involved reduction of the undissociated acid or salt. The reviewer does not agree, however, that one of the first steps in the reduction of sulphuric acid by copper at 200° is the formation of cupric oxide, p. 249.

"Certain bacteria, the *begeatoa*, make use of sulphur as a source of energy. They absorb hydrogen sulphide, which they oxidize to sulphur. The sulphur accumulates in the organisms and furnishes energy by being oxidized to sulphuric acid as the need arises," p. 229.

"Solutions of sulphites oxidize very slowly when the sulphite is extremely pure. The reaction is catalyzed to an extraordinary extent by certain catalysts, of which the cupric ion is the most effective. No other example is known of a catalyst acting at so low concentrations. One gram-ion of copper in a billion tons of hundredth-normal sulphite solution increases the rate of reaction one-third. Certain substances, such as sugar and the phenols, paralyze this reaction," p. 251.

"Violet phosphorus is a crystalline solid, insoluble in all solvents and unchanged in the air. It has no odor, does not phosphoresce, and is non-toxic. Its volatility is much less than that of white phosphorus, the vapor pressure being only about 4 cm at 290°, rising to 43.2 atm. at 592.5°. The violet phosphorus melts at this temperature, this being the triple point. The melted violet phosphorus is pale yellow and the study of the vapor

pressure curve shows the liquid to be identical with that obtained by melting white phosphorus. . . . Below 44.5° this liquid phosphorus changes into a metastable form, white phosphorus," p. 339.

At red heat the vapor density of metaphosphoric acid corresponds to the formula $H_2P_2O_6$, p. 357, and consequently all one can say about metaphosphoric acid at room temperature is that it has the formula $(HPO_3)_n$, p. 359. "It is more than probable that the glacial acid, which is vitreous and amorphous, is a mixture of several more or less complex acids, which may be the reason why it does not crystallize," p. 360.

The author is inclined to believe that active nitrogen is monatomic, electrically neutral, nitrogen, p. 278, and he is convinced that nascent hydrogen is monatomic, electrically neutral, hydrogen, p. 86, and yet he attributes the diffusion of hydrogen through heated platinum as due to the formation of an instable compound, p. 84, and accounts for the catalytic action of platinum black on oxyhydrogen gas by the intermediate formation of PtO which reacts with hydrogen, p. 97. Platinous hydroxide is said by Wöhler to react autocatalytically with hydrogen, p. 761; but one wonders whether traces of platinum are not essential.

The reviewer is a little sceptical as to the formation of mellitic acid by the oxidation of pure graphite, p. 386. The best evidence seems to the reviewer to indicate that the mellitic acid comes from oxidation of the hydrocarbon impurities in the graphite. It would be interesting to know if one could get mellitic acid by oxidizing graphite obtained from diamond. A less expensive experiment would be to give powdered graphite an extensive steam treatment and then see if one could get mellitic acid from it. As a preliminary step one might study the action of permanganate on activated charcoal.

On p. 180 the author says that iodine reacts with a concentrated potassium chlorate forming iodate and setting free chlorine

$$2KClO_3 + I_2 = K_2I_2O_6 + Cl_2.$$

The chlorine is not set free as such but oxidizes the excess iodine to iodic acid. It seems to the reviewer that it is much more likely that potassium chlorate oxidizes iodine to iodic acid, going down itself to chloride. In view of the fact that potassium perchlorate has the formula $KClO_4$, one would like to know why barium periodate has the formula $Ba_5(IO_6)_2$ and what its apparent molecular weight is in aqueous solution.

The author considers the passivity of aluminum, iron and chromium as due to an oxide film, though he seems to consider that nitric oxide plays some part with iron, p. 318. For some reason that is not quite clear, he wishes to ascribe passivity in presence of other acids to other causes, perhaps because he does not see how there can be oxidation.

"We shall see later that the value of the osmotic pressure may be quite large; in a normal solution of sugar at 0° the osmotic pressure is 22 atmospheres. Nevertheless it is impossible to recognize its influence on the walls of the vessels. It seems at first sight strange that a phial or a thin-walled flask should not break under the pressure of the dissolved sugar when filled completely with sugar and water. This difficulty is easily got round if one remembers that the outer film of a liquid is the seat of a centripetal force, tending to reduce the volume of the liquid and whose intensity is measured in thousands of atmospheres. The osmotic pressure disappears completely in comparison with the surface tension; the outer layer of the liquid, whether in contact with air or with a solid, therefore constitutes a shell whose resistance to extension is so great that the dilating effect of the osmotic pressure cannot manifest itself." p. 186.

This sounds plausible but what would be the answer if one asked about the osmotic pressure of the water dissolved in the sugar, which can easily amount to thousands of atmospheres? Also what would happen supposing either osmotic pressure of a solution should become larger than the so-called internal pressure? That is an interesting problem which nobody has faced so far as the reviewer knows; but which is a problem in physical chemistry rather than in inorganic chemistry.

Wilder D. Bancroft

Essays on the Art and Principles of Chemistry. *By Henry E. Armstrong. 22 × 15 cm; pp. xxxi + 276. New York: The Macmillan Company, 1927. Price: $4 50.* The essays are entitled: the art and principles of chemistry; a dream of fair hydrone; the thirst of salted water; the corrosion of iron and other metals; first Messel memorial lecture; the origin of osmotic effects; electrolytic conduction.

Mr. Armstrong is not an accurate person. He says, p. xiv, that Ostwald's *Zeitschrift für physikalische Chemie* first appeared in 1884, whereas he means 1887. Also the Germans of that date did not write adjectives with a capital as Mr. Armstrong does. On p. 26 he says: "Progress has not always been premeditated but has often been the outcome of some happy accident to a shrewd observer. Such was the case when Galvani (1779) noticed that a frog's leg was caused to twitch when pieces of two different metals touching at the one end were placed, some distance apart, upon the bared muscles: hence arose the discovery of what became known as the Galvanic current. Soon afterwards (1780), Volta constructed his electric pile, consisting of alternate discs of copper and zinc separated by discs of paper moistened with a solution of salt."

Galvani's discovery was made in 1791 and not in 1779. Galvani himself thought that it was essential to touch the muscles and the nerves, not the muscles alone. Armstrong is reading into Galvani's experiments what was actually discovered by Volta. The voltaic cell cannot be forced back of 1792 and the pile was discovered in 1800, twenty years after Armstrong's hypothetical date. Instead of the first battery being definitely copper and zinc, it was copper, brass or better silver and tin or better zinc. The battery which Volta actually described in his letter to Banks was silver and zinc. Armstrong is very keen about people reading Faraday's Experimental Researches in Electricity; but on p. 27 he uses the German spelling of cathode and cation, which Faraday does not do in the edition which the reviewer owns. Can it be possible that this is a survival of Kolbe's influence?

On p. 39 we read that "it is customary, in the text-books, to speak of forms of carbon other than the diamond—to wit, graphite and the charcoal carbons. No proof has yet been given that these are carbon—much may be said in favour of the view that they are but highly condensed hydrocarbons." If Mr. Armstrong has any evidence to prove that the diamond will not change to graphite when heated in the absence of hydrogen, he should not withhold it.

Another case of careless misstatement is to be found on p. 47. "The generalisation [of Arrhenius] came at a time when much attention was being paid to the determination of molecular weights of dissolved substances. Raoult especially had shown that equimolecular proportions of many substances produced the same effect upon the properties of a solvent: for example in raising the boiling-point." Raoult did an enormous amount of work on freezing-points and some work on the lowering of vapor pressures at constant temperatures; but the reviewer does not recall any boiling-point measurements at least prior to 1890. Of course, this is of no real importance in itself. Armstrong could have said "lowering the freezing point" instead of "raising the boiling point"; but this illustrates the general inaccuracy which is characteristic of all his writings.

A slightly different case occurs on p. 51 when discussing the effect of solutes on the properties of the solvent. "How, in particular, is the peculiar and enhanced effect of (potential) electrolytes as compared with non-electrolytes to be pictured? The first assumption that may be made is—that, in liquids, the primary, chemically active unit is the simple molecule. In water this is hydrone, OH_2. [Hydrol is a better term and is not used by Armstrong.] 'It will easily be granted that water is saturated with hydrone, the proportion varying with the temperature. As a matter of fact, the vapour pressure of an aqueous solution is lower than that of water."

Armstrong knows, or ought to know, that the dissolving of any substance in any liquid will lower the partial pressure of that liquid, regardless whether the liquid does or does not contain polymerized molecules. That makes no difference to Armstrong. He is apparently perfectly willing to make a misleading statement provided he scores thereby.

A typical instance of this sort occurs on p. 45. "*Common* water will convey or conduct an electric current—electrolytically. The more it be purified, the less readily it conveys

the current. *It is logical to assume that water free from every contamination would be a non-conductor.*" It is legitimate to make such an assumption; but it is not a logical necessity as Armstrong implies. The hyperbola always approaches the asymptote but never reaches it. There is nothing in the nature of things to prevent theoretically pure water from having an electrolytic conductivity of its own, and many people believe that it does have. That does not fit in with Armstrong's personal views, so he adopts these rather unsportsmanlike tactics.

One could go on like this throughout the book; but even this is probably too much. Armstrong is a brilliant and versatile man who has had many good ideas; but who has never had the slightest conception of what constitutes proof. Consequently, his good ideas have been no more successful than his poor ones. In fact, he says, rather pathetically on p. xxx that "having no Ostwald, I must act as my own interpreter." If he had had an Ostwald, he might have accomplished very much—always assuming that he could have kept on speaking terms with the hypothetical Ostwald.

Armstrong has emphasized for years the fact that water is "a mixture of various, liquid components, of polyhydrones $(H_2O)_x$, $(H_2O)_y$, etc., saturated with the gas hydrone, OH_2, the proportion of the constituents depending upon the temperature," p. 36. He has not only never done anything with this conception; but he has not even detected the fallacy in the reasoning of the physicists that the lowering of the temperature of the maximum density by salts proves that the salts displace the equilibrium toward the depolymerized form. Since he abominates the electrolytic dissociation theory, he is barred from explaining the 'neutral salt effect' or the Hofmeister series as due to displacement of the water equilibrium. After all these years he has worked out no method for telling in which direction a given substance displaces the water equilibrium or whether substance A displaces it more or less than substance B.

It is not much of an exaggeration (cf. pp. 36, 38, 51, 133, 136, 159, 260, 265, 276) to say that about all that he has worked out about water is contained in the following quotation, p. 37. "Bring hydrogen and oxygen together, in presence of the necessary negotiators of change, allow them to interact in the sense of the equation,

$$2\,H_2 + \epsilon\delta\kappa + O_2 = 2H_2O + \epsilon\delta\kappa$$

they give rise to hydrone and eventually to water. These products differ in an astounding way from their generators. The molecule of hydrone has little more than half the mass of that of oxygen, yet—given proper conditions—it condenses, with the greatest ease, to water. Not only so, the amount of energy set free in the interaction of the molecules of hydrone: $xOH_2 = (OH_2)_x$, is about one-tenth of that liberated in the original gaseous interaction. The molecules of hydrone are thus shown to be possessed of residual affinity in a far higher degree than is even oxygen. Hydrone, indeed, may be said to be a really active form of oxygen-stuff—far more so than is gaseous oxygen. Hence it is that water is so good a solvent: at least, there are molecules in the liquid mass which are very active, chemically speaking. Water, we shall see, must be regarded as a complex mixture, in which are present molecules of varying degrees of complexity: H_2O, $(H_2O)_x$, $(H_2O)_y$, etc., in proportions which depend upon temperature."

Armstrong's early work on the reduction of nitric acid was very good; but he could not finish it because he never would learn about overvoltages, etc. Armstrong recognized the unsatisfactory side to the use of volume concentrations; but the paragraph on the subject, p. 54, is not helpful. "The conclusions deduced by studying solutions made by dissolving substances all to the same volume—a method in no way comparable with that involved in dealing with equal volumes of gases—are obviously not comparable, as the molecular proportions in which solute and solvent are present will vary more or less, according to the nature of the dissolved substance. Most of the peculiarities to which attention has been directed are traceable to this illogical practice. Only the very dilute solutions prepared in this manner will afford comparable results. On the other hand, if the molecular proportions of solvent and solute be kept constant, there is always the difficulty that the ultimate volumes vary—that the volume occupied within the solvent by the solute is subject to

variation. In fine, it would seem to be impossible to make any strict comparison of solutions—the conclusions must always be open to many corrections."

The inaccuracy of his conception of proof is shown clearly on p. 261. "If any substance be dissolved in water, the physical properties of the liquid are proportionately altered, not always in the same molecular ratio but to an extent which depends upon the nature of the compound dissolved; potential electrolytes produce the greater effect per molecule. Apparently, the effect is in no way mechanical, *i.e.*, solvent and solute do not merely become mixed together and the molecules separated by mutual (mechanical) interference; the process is inductive and chemical throughout.

"Non-electrolytes all produce the same effect per molecule, whatever their molecular magnitude, in raising the osmotic attractive power of water and, at the same time, of lowering its vapour pressure. The negative pressure developed within the liquid is such that apparently a gramme-molecular-proportion of hydrone is *taken out of action as volatile constituent* per gramme-molecular-proportion of the *non-electrolyte* dissolved; each molecule of the solute appears to "anchor" a molecule of hydrone, yet in some special way which enables this still to preserve its attractive power for molecules of its own kind. The effect of potential electrolysis is greater, to an extent depending upon the valency and character of the constituent radicles; "salts" of the type X′R′, in very dilute solution, may produce an effect double that proper to a single molecule and the effect of salts containing radicles of higher valency than unity may be still greater," p. 261.

The formula for the change of vapor pressure of the solvent with the concentration and molecular weight of the solvent was worked out quantitatively by van't Hoff both in an exact and in a simplified form for all solutes in all solvents, including such different cases as benzene, water, and acetic acid. All Armstrong can do is to say that "apparently a gramme-molecular-proportion of hydrone is *taken out of action as volatile constituent* per gramme-molecular-proportion of the *non-electrolyte* dissolved." He has not deduced anything. He has merely stated an experimental observation which is not generally true. The formula which Armstrong does not give applies to liquids like benzene which are presumably not polymerized, to water and alcohol, which are not polymerized appreciably as vapors but are as liquids, and to acetic acid which is polymerized both as vapor and as liquid. There is nothing in what Armstrong has said to show what molecular weight should be used for N in the case of acetic acid. In other words Armstrong is not as far along today as van't Hoff was over forty years ago. Nobody knows whether Armstrong could evaluate the factors on which the lowering of the freezing-point depends. He never has done so even with van't Hoff's work before him. Nobody believes that he could have discovered them—as van't Hoff did.

One more illustration will complete the indictment. Armstrong postulates, p. 260, that "not only are electrolysis and chemical change inseparable effects—the conditions which determine the one inevitably involve the other—but that change takes place and only takes place in a system of three components, such as is known to constitute a voltaic couple." It is quite possible that this is true; but this theory has never been put in a form which has been understood by anybody, so far as the reviewer can learn, and it has not yet proved useful in any way. Armstrong considers that the experiments of H. B. Baker are a brilliant confirmation of this theory; but this may also be taken as a justification of the reviewer's criticism.

Another interesting thing about this book is that Armstrong apparently thinks that he writes good English.

Wilder D. Bancroft

BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS ORSAY

BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS - ORSAY

ÉCOLE DE CHIMIE INDUSTRIELLE 28, rue St-Dominique PARIS (7e) ANNULÉ

NAME INDEX

To Papers

Agel, F. E., See Papish and Agel,..... 1746
Amick, C. A., The Copper Number for Glucose,..... 1441
Andrews, J. C., and F. P. Worley, Mutarotation. I-III,.....742, 882, 1880
Ashton, F. W., See Hansen, Dyckerhoff, Ashton and Bogue,..... 607
Bancroft, Wilder D., The Mass Unit of the Chemical Potential,..... 69
Bancroft, Wilder D., Gibbs on Adsorption,..... 1501
Bancroft, Wilder D., and Charles Gurchot, Cell Mitosis,..... 430
Bancroft, Wilder D., and C. W. Tucker, Gibbs on Emulsification,..... 1681
Baughman, I. P., The Study of the Tannin-Gelatin Reaction,..... 448
Bell, Thomas, and Robert Wright, The Partial Vapor Pressures of Benzene-Toluene and Benzene-Ethylene Mixtures,..... 1886
Bennett, A. N. C., Some Vapor Pressures and Activities of Aqueous Solutions of Sodium Silicates,..... 890
Bergstein, Milton, The Catalytic Minimum Point. II,..... 178
Bigelow, S. L., and H. M. Trimble, The Relation of Vapor Pressure to Particle Size,... 1798
Bogue, R. H., See Hansen, Dyckerhoff, Ashton and Bogue,..... 607
Bogue, R. H., See Lerch and Bogue,..... 1627
Botts, E. D., and F. C. Krauskopf, Some Electrochemical Studies of Titanium,..... 1404
Bowe, L. E., The Neutral Salt Effect,..... 291
Brewer, F. M., Germanium. XXIV,..... 1817
Brewer, F. M., and L. M. Dennis, Germanium. XIX, XXII,.....1101, 1526
Brown, O. W., See Madenwald, Henke and Brown,..... 862
Bruzs, B., Corresponding States for the Entropy of Elements, 681
Burk, Dean, Photosynthesis with Ammonia,..... 1338
Burk, R. E., A Gage for the Measurement of High Vacua,..... 591
Bush, Florence, The Color of Silver Chromate,..... 931
Cantelo, R. C., The Methane Equilibrium. II-IV, ...124, 246, 417
Carpenter, D. C., The Influence of Salts on the Optical Rotation of Gelatin. I,..... 1873
Carroll, B. H., and Donald Hubbard, The Photographic Emulsion. I,..... 906
Chaffee, Clare S., See Parks and Chaffee,..... 439
Chakravarti, M. N., and N. R. Dhar, Studies in Adsorption. XIX,..... 997
Chandler, W. L., and E. J. Miller, Colloidal Iodine,..... 1901
Colins, P. G., and H. V. Tartar, A Laboratory Study of Nitrogen Fixation by the High-Tension Arc,..... 1539
Collins, S. C., A New Thermoregulator,..... 1097
Cooper, E. A., and Edgar Saunders, On the Relation of Phenol to Proteins and other Colloids,..... 1
Coste, J. H., On the Solubility of Pure and Atmospheric Nitrogen in Distilled and Sea Water,..... 81

Dawson, H. M., The Signification of Isocatalytic Data and the So-called Protion Theory of Chemical Reactivity,.... 1400

Dennis, L. M., and S. M. Joseph, Germanium. XXIII,..... 1716
Dennis, L. M., See Brewer and Dennis,.....1101, 1526
Dennis, L. M., See Tressler and Dennis,..... 1429
Denslow, R. R., See Taylor and Denslow,..... 374
Dew, W. A., and H. S. Taylor, Adsorption and Heats of Adsorption of Ammonia Gas on Metallic Catalysts,..... 277
Dexter, S. T., See Kraemer and Dexter,..... 764
Dhar, N. R., Relation Between the Metabolism of Glucose and Fats in Diabetes,..... 1259

Dhar, N. R., See Chakravarti and Dhar,..... 997
Dhar, N. R., See Ghosh and Dhar,.....187, 649
Dodd, L. E., A Method for comparing the Times of Mixing of Two Transparent Liquids in Different Proportions and Some Experimental Results, particularly with Gasoline and Carbon Bisulphide,.... 1761

Dow, Miss I. C., See Smith and Dow,..... 1263
Dyckerhoff, W., See Hansen, Dyckerhoff, Ashton and Bogue,..... 607
Eckert, T. S., and W. G. France, The Effect of Gelatin upon the Size and Distribution of Macroscopic Crystals grown from Aqueous Solutions,..... 877

Fall, P. H., Detergent Action of Soaps,..... 801
Fells, H. A. and J. B. Firth, The Function of Water present in Silicic Acid Gel, 1230
Ferguson, J. B., The System Water-Phenol,..... 757
Ferguson, John, See McBain and Ferguson,..... 564
Firth, J. B., See Fells and Firth,..... 1230
France, W. G., See Eckert and France,..... 877

Frazer, J. C W., W. A. Patrick and H. E. Smith, The Thickness of Adsorbed Vapor Films,..... 897
Frazer, J. C. W., See Patrick, Frazer and Rush,..... 1511
Frazier, W. R., See Scott and Frazier,..... 459
Funnell, W. S., and G. I. Hoover, An All-Glass Gas Circulating Apparatus,..... 1099
Ganguly, P. B., Diffusion of Aqueous Sodium Silicate Solutions across Semipermeable Membranes, ... 407

Ganguly, P. B., Studies in the Formation of Liesegang Rings,..... 481
Garner, W. E., D. McKie and B. C. J. G. Knight, The Area of the Internal Surface of Charcoal as determined by the Adsorption of Normal Aliphatic Alcohols from Aqueous Solution,..... 641

Garrison, A. D., See Weiser and Garrison,..... 1237
Geddes, J. R., See Gerke and Geddes,..... 886
Gerke, R. H., and J. R. Geddes, An Improved Hydrogen Electrode Vessel and the Electromotive Force of the Mercury, Mercurous Bromide, Bromide Ion Electrode,..... 886

Getz, Dorothy, See Rice and Getz,..... 1572
Ghosh, S., and N. R. Dhar, Studies in Adsorption. XVII, XVIII,.....187, 649
Gibbs, H. D., Phenol Tests. IV,..... 1053
Gibson, R. E., The System Sodium Sulphate-Water..... 496
Gilbert, E. C., The Effect of Higher Aliphatic Acids on the Surface Tension of a Heavy Hydrocarbon Oil,..... 543

Gilbert, E. C., and B. E. Lauer, A Study of the Ternary System: Methyl Benzoate, Methanol, and Water,..... 1050

Gilligan, G. M.,	See Holland and Gilligan,	728
Glockler, George,	Ionization produced by Radon in Spherical Vessels,	1322
Gortner, R. A., Walter F. Hoffman,	The Imbibition of Gelatin dried as a Gel and as a Sol,	464
Gray, L. T. M.,	Studies in the Experimental Technique of Photochemistry. IV,	1732
Gronwall, T. H.,	See LaMer and Gronwall,	393
Gurchot, Charles,	See Bancroft and Gurchot,	430
Guthrie, F. C.,	See Keffler and Guthrie,	58
Halvorson, H. G., and R. L. Starkey,	Studies on the Transformation of Iron in Nature. I,	626
Hann, R. M., and G. L. Keenan,	The Optical Identification of the Naphthalene Sulphonic Acids by means of their Benzyl-Pseudo-Thiourea Salts,	1082
Hansen, W. C., W. Dyckerhoff, F. W. Ashton, R. H. Bogue,	Studies on the System Lime-Alumina-Silica,	607
Harman, R. W.,	Aqueous Solutions of Sodium Silicates. V-VII,	355, 511, 616
Hartley, H. B.,	See Wolfenden, Jackson and Hartley,	850
Hatschek, Emil,	The Apparent Viscosity of Colloidal Solutions,	383
Henke, C. O.,	See Madenwald, Henke and Brown,	862
S. B. Hendricks, and R. W. G. Wyckoff,	The Positions of the K-Absorption Limits of Vanadium in various of its Compounds,	703
Hildebrand, J. H.,	See Scarlett, Morgan and Hildebrand,	1566
Hoffman, Walter F.,	See Gortner and Hoffman,	464
Holland, E. B., and G. M. Gilligan,	Solubility of Copper Sulphate, Malachite, and Burgundy Precipitate in Ammonium Hydroxide, Carbonate and Bicarbonate,	728
Hoover, G. I.,	See Funnell and Hoover,	1099
Howes, H. S.,	See McBain, Howes and Thorburn,	131
Hubbard, Donald,	See Carroll and Hubbard,	906
Huffman, H. M.,	See Parks and Huffman,	1842
Jackson, W.,	See Wolfenden, Jackson and Hartley,	850
Jones, E. R.,	Some Observations on the System Phenol-Water,	1316
Joseph, S. M.,	See Dennis and Joseph,	1716
Keenan, G. L.,	See Hann and Keenan,	1082
Keffler, L. J. P., and F. C. Guthrie,	Investigation on the Heats of Combustion of Proposed Secondary Standard Substances and on Position and Optical Isomers,	58
Kilpatrick, M. L.,	See Rice and Kilpatrick,	1507
Kleeman, R. D.,	The Absolute Zero of the Externally Controllable Entropy and Internal Energy of a Substance or Mixture,	747
Kleeman, R. D.,	Properties of Substances and Mixtures in the Condensed State at the Absolute Zero of Temperature,	937
Kleeman, R. D.,	Properties at the Absolute Zero of Temperature of the Quantities associated with the Reversible Mixing of Substances,	1559
Kleeman, R. D.,	The Internal Energy, Maximum Work, and Free Energy of the Elements,	1669
Knight, B. C. J. G.,	See Garner, McKie and Knight,	641
Kohman, G. T.,	See Lowry and Kohman,	23
Kraemer, E. O., and S. T. Dexter,	The Light-Scattering Capacity (Tyndall Effect) and Colloidal Behavior of Gelatin Sols and Gels,	764

Krauskopf, F. C.,
Laird, F. W.,
Lambert, R. H., and E. P. Wightman,
See Botts and Krauskopf,..... 1404
Sedimentation of Colloidal Particles,..... 1034
Thermodynamic Possibilities of the Silver Sulphide Bromine-Acceptor Hypothesis of Latent Image Formation,..... 1249

LaMer, V. K., and T. H. Gronwall,
The Partial Molal Volumes of Water and Salt in Solutions of Alkali Halides,..... 393

Langmuir, D. B.,
See Langmuir and Langmuir,..... 1719

Langmuir, Irving, and D. B. Langmuir,
The Effect of Monomolecular Films on the Evaporation of Ether Solutions,..... 1719

Latimer, W. M.,
The Electrode Potentials of Beryllium, Magnesium, Calcium, Strontium, and Barium from Thermal Data,..... 1267

Lauer, B. E.,
See Gilbert and Lauer,..... 1050

Lee, W. B.,
See McBain and Lee,..... 1674

Leighton, Alan, and O. E. Williams,
The Basic Viscosity of Ice-Cream Mixes,..... 596

Leighton, Alan, and O. E. Williams,
The Effect of Temperature on the Basic Viscosity of Ice-Cream Mixes,..... 1663

Lenher, Sam, and I. R. McHaffie,
The Free Energy Change in Adsorption of a Solid-Vapor Interface,..... 719

Lerch, William, and R. H. Bogue,
Studies on the Hydrolysis of Compounds which may occur in Portland Cement,..... 1627

Lowry, H. H., and G. T. Kohman,
The Mechanism of the Absorption of Water by Rubber,..... 23

Lowry, H. W., and P. S. Olmstead,
The Adsorption of Gases by Solids with special reference to the Adsorption of Carbon Dioxide by Charcoal..... 1601

Lynn, George,
A Convenient Form of Apparatus for the Determination of Melting Temperature,..... 1381

McBain, J. W., and John Ferguson,
On the Nature of the Influence of Humidity Changes upon the Composition of Building Materials,... 564

McBain, J. W., H. S. Howes, Muriel Thorburn,
The Hydrogen Electrode in the Study of the Rate of Saponification of Oils and Fats by Aqueous Alkali,..... 131

McBain, J. W., and W. B. Lee,
Adhesives and Adhesion: Gums, Resins and Waxes between Polished Metal Surfaces,..... 1674

McHaffie, I. R.,
See Lenher and McHaffie,..... 719

McKie, D.,
See Garner, McKie and Knight,..... 641

Madenwald, F. A., C. O. Henke, O. W. Brown,
Catalytic Activity of Lead,..... 862

Maeda, Tutomu,
Some Remarks on the Colloidal Theory of Cements, 933

Martin, F. D.,
See Mellon and Martin,..... 161

Mason, C. W.,
Structural Colors in Insects. II, III,.....321, 1856

Mellon, M. G., and F. D. Martin,
Solutions for Colorimetric Standards. I,..... 161

Miller, E. J.,
Adsorption from Solution by Ash-free Adsorbent Charcoal. III,..... 1197

Miller, E. J.,
See Chandler and Miller,..... 1091

Mokrushin, S. G.,
On the Contraction of Molecules in the Liquid State, 1581

Morgan, W. L.,
See Scarlett, Morgan and Hildebrand,..... 1566

Morris, V. N., L. H. Reyerson,
The Catalytic Activity of Metallized Silica Gels. I, II,.....1220, 1332

Morton, R. A., and R. W. Riding,
The Refractivity of Carbon Monoxide,..... 723

Nord, F. F.,	Influence of Heat and Hydrogen Ion Concentration on Biological Transportation Systems containing Sulphur,	867
Nutting, P. G.,	The Adsorptive Force of Silica for Water,	531
Olmstead, P. S.,	See Lowry and Olmstead,	1601
Papish, Jacob, and F. E. Agel,	Composite Yellow,	1746
Parks, G. S., and Clare S. Chaffee,	Some Physical Chemical Properties of Mixtures of Acetone and Isopropyl Alcohol,	439
Parks, G. S., and H. M. Huffman,	Studies on Glass. I,	1842
Patrick, W. A., J. C. W. Frazer, R. I. Rush,	A Study of the Structural Changes in Amorphous Materials. Silica Gel.,	1511
Patrick, W. A.,	See Frazer, Patrick and Smith,	897
Patton, I. J.,	See Waldbauer and Patton,	1433
Peacock, D. H.,	The Velocity of Reaction and Energy of Activation of Halogen Compounds,	535
Pearce, J. N., and R. D. Snow,	An Improved Dynamic Method for measuring Vapor Pressures,	231
Perry, J. H.,	The Vapor Pressures of Methylene Chloride,	1737
Pickett, C. F.,	See Taylor and Pickett,	1213
Pitts, C. R.,	The Ionization obtained by bubbling Air through Various Solutions,	693
Porter, E. E.,	See Weiser and Porter,	1383, 1704, 1824
Pound, J. R.,	The Electrical Conductivities of Some Solutions in Aniline,	547
Reiff, O. M.,	See Rice and Reiff,	1352
Reid, E. E.,	Fifth Report of the Committee on Contact Catalysis,	1121
Reinhard, M. C.,	See Riegel and Reinhard,	713
Reyerson, L. H., and L. E. Swearingen,	The Adsorption of Gases by Metallized Silica Gels,	88
Reyerson, L. H.,	See Morris and Reyerson,	1220, 1332
Rice, F. O., and Dorothy M. Grtz,	A Study of the Thermal Decomposition of Nitrogen Pentoxide,	1572
Rice, F. O., and M. L. Kilpatrick,	The Photochemical Decomposition of Hydrogen Peroxide Solutions,	1507
Rice, F. O, and O. M. Reiff,	The Thermal Decomposition of Hydrogen Peroxide,	1352
Rice, O. K.,	Dynamic Surface Tension and the Structure of Surfaces,	207
Riding, R. W.,	See Morton and Riding,	723
Riegel, E. R, and M. C. Reinhard,	The Zone Pattern formed by Silver Dichromate in Solid Gelatine Gel,	713
Rush, R. I.,	See Patrick, Frazer and Rush,	1511
Sanders, Edgar,	See Cooper and Sanders,	1
Scarlett, A. J., W. L. Morgan, and J. H. Hildebrand,	Emulsification of Solid Powders,	1566
Scott, A. F., and W. R. Frazier,	The Solubilities and Densities of Saturated Solutions of Sodium and Potassium Halides at 25°,	459
Sen, K. C.,	Adsorption by Metallic Hydroxides. I-V,	419, 525, 686, 922, 1840
Smith, H. E.,	See Frazer, Patrick and Smith,	897

Smith, R. C., and Miss I. C. Dow,	The Drop Number and Emulsifiability,	1263
Snow, R. D.,	See Pearce and Snow,	231
Soper, F. G.	The Rate of Transformation of Acetylchloroaminobenzene into o- and p-Chloroanilides as a measure of the Catalytic Power of Hydrochloric Acid,	1192
Soper, F. G.,	The Velocity of Interaction of Ions,	1790
Starkey, R. L.,	See Halvorson and Starkey,	626
Stranathan, J. D., and John Strong,	Viscosities, Electrical Conductivities, and Specific Volumes of Acetic Acid-Stannic Chloride Solutions,	1420
Strong, John,	See Stranathan and Strong,	1420
Swan, Enoch, and A. R. Urquhart,	Adsorption Equations,	251
Swearingen, L. E.	See Reyerson and Swearingen,	88
Sweitzer, C. W.,	Light-Scattering of Aqueous Salt Solutions,	1150
Tartar, H. V.,	See Colin and Tartar	1539
Taylor, H. A., and R. R. Denslow,	The Thermal Decomposition of Nitrosyl Chlorides,	374
Taylor, H. A.,	The Decay of Phosphorescence of Zinc Sulphide,	115
Taylor, H. A., and C. F. Pickett	The Decomposition of Hydrogen Sulphide,	1212
Taylor, H. A., and W. A. Wesley,	The Gaseous Reaction between Hydrogen Sulphide and Sulphur Dioxide,	216
Taylor, H. S.,	See Dew and Taylor,	277
Taylor, P. B.,	Electromotive Force of the Cell with Transference and Theory of Electrolytes,	1478
Trimble, H. M.,	See Bigelow and Trimble,	1798
Trimble, H. M.,	The Coalescence of an Unfilterable Precipitate of Barium Sulphate,	601
Thorburn, Muriel,	See McBain, Howes and Thorburn,	131
Tressler, K. M., and L. M. Dennis,	Germanium. XX,	1429
Tucker, C. W.,	A Study of Photovoltaic Cell,	1357
Tucker, C. W.,	See Bancroft and Tucker,	1681
Urquhart, A. R.,	See Swan and Urquhart,	251
Venkateswaran, S.,	Compressibilities of Aqueous Solutions of Some Fatty Acids,	1521
Vincent, G. P.,	Detergent Action of Soaps. II,	1281
Waldbauer, L. J., and I. J. Patton,	On the Nature of Activated Molecules,	1433
Walker, H. W.,	Catalytic Reactions of Ethylene,	961
Washburn, E. R.,	The Creeping of Solutions,	1246
Weiser, H. B., and A. D. Garrison,	The Role of Water in the Photo-chemical Decomposition of Zinc Sulphide,	1237
Weiser, H. B., and E. E. Porter,	The Physical Chemistry of Color Lake Formation. I-III,	1383, 1704, 1824
Wesley, W. A.,	See Taylor and Wesley,	216
Wightman, E. P.,	See Lambert and Wightman,	1249
Williams, J. W., and T. A. Whitenack,	The Application of the Electron Tube to Potentiometric Titrations,	519
Williams, O. E.,	See Leighton and Williams,	596, 1663

Wolfenden, J. H., W. Jackson, and H. B. Hartley, Heats of Ionization in Methyl Alcohol,..... 850
Wood, Lyman J., A Study of Annealing Effects of Certain Copper-Nickel Aluminum-Manganese Alloys,..... 1693
Woodman, R. M., On the Causes of Solubility,..... 1742
Worley, F. P., See Andrews and Worley,.....742, 882, 1880
Wright, Robert, The Partial Vapor Pressures of Benzene-Toluene and Benzene-Ethylbenzene Mixtures,..... 1886
Wyckoff, R. W. G., See Hendricks and Wyckoff,..... 703
Wynne-Jones, W. F. K., The Correction of Conductivity Data for the Conductivity of the Solvent,..... 1647

BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS - ORSAY

BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS
ORSAY

NAME INDEX

To New Books

Ambronn, Hermann, and Albert Frey,	Das Polarisationsmikroskop, seine Anwendung in der Kolloidforschung und in der Färberei,	477
Andrade, E. N. da C.,	The Structure of the Atom,	1272
Armstrong, H. E.,	Essays on the Art and Principles of Chemistry,	1890
Bancroft, W. D.,	Applied Colloid Chemistry,	157
Benrath, Alfred,	Physikalische Chemie, Part II,	1278
Bernard, Claude,	An Introduction to the Study of Experimental Medicine,	1435
Blasdale, W. C.,	Equilibria in Saturated Salt Solutions,	1758
Bligh, N. M.,	The Evolution and Development of the Quantum Theory,	639
Bridgman, P. W.,	A Condensed Collection of Thermodynamic Formulas,	479
Bodansky, Meyer,	Introduction to Physiological Chemistry,	1106
Brockman, C. J.,	Electro-Organic Chemistry,	1117
Caven, R. M.,	Gas and Gases,	1439
Cohen, Ernst,	Physico-Chemical Metamorphosis and Some Problems in Piezochemistry,	1593
Dean, Reginald S.,	Theoretical Metallurgy,	318
Deming, Horace,	General Chemistry,	792
Deming, H. G., and S. B. Arenson,	Exercises in General Chemistry and Qualitative Analysis,	1120
Eggert, John,	Lehrbuch der physikalischen Chemie in elementarer Darstellung,	316
Einstein, Albert,	Investigations on the Theory of the Brownian Movements,	960
Eitel, Wilhelm,	Physikalisch-chemische Mineralogie und Petrologie,	159
Elsdon, G. D.,	Edible Oils and Fats,	479
Ettele, Claude,	Lubricating Oil Salesman's Primer,	477
Findlay, Alexander,	Einführung in die Phasenlehre und ihre Anwendungen,	480
Finter, F. B.,	An Introduction to Physical Chemistry,	640
Fischer, Joseph,	Die Verstäubungserscheinungen bei Metallen,	1276
Friend, J. Newton,	A Text-Book of Inorganic Chemistry, Vol. IX, Part II,	1755
Geiger, H., and Karl Scheel, Editors,	Handbook der Physik, Vol. X,	474
Gillett, H. W., and E. L. Mack,	Molybdenum, Cerium and Related Alloy Steels,	145
Haas, Arthur,	Introduction to Theoretical Physics, Vol. II,	147
Hale, W. J., Editor,	A Survey of American Chemistry,	1278
Harden, Arthur,	Alcoholic Fermentation,	158
Hedges, E. S., and J. E. Meyers,	The Problem of Physico-Chemical Periodicity,	638
Hinshelwood, C. N.,	Thermodynamics for Students of Chemistry,	635
Höber, Rudolf,	Physikalische Chemie der Zelle und Gewebe,	154
Howe, H. E.,	Chemistry in the World's Work,	151
Kaye, G. W. C., and T. H. Laby,	Physical and Chemical Constants and Some Mathematical Functions,	320

Köhler, August,	Die Verwendung des Polarisationsmikroskops für biologische Untersuchungen,	798
Loeb, L. B.,	Kinetic Theory of Gases,	1588
Lorenz, Richard, and Wilhelm Eitel,	Pyrosole,	959
MacDougall, F. H.,	Thermodynamics and Chemistry,	797
Mellor, J. W.,	A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. VII,	783
Meyer, R. J., Editor,	Gmelins Handbuch der anorganischen Chemie, Parts I, V, XIII	475, 640, 800
Mullin, C. E.,	Acetate Silk and its Dyes,	1748
Needham, Joseph, Editor,	Science, Religion and Reality,	303
de Noüy, P. LeComte,	Surface Equilibria of Biological and Organic Colloids,	1270
Oppenheimer, Carl,	Lehrbuch der Enzyme,	1274
Ostwald, Wolfgang,	Practical Colloid Chemistry,	799
Planck, Max,	Treatise on Thermodynamics,	1275
Plimmer, R. H. A.,	Practical Organic and Biochemistry,	1273
Rastall, R. H.,	Physico-Chemical Geology,	1280
Reilly, J., W. N. Rae and T. S. Wheeler,	Physico-Chemical Methods,	955
Reymond, Arnold,	History of the Sciences in Greco-Roman Antiquity,	1594
Rideal, E. K.,	An Introduction to Surface Chemistry,	632
Rideal, E. K., and H. S. Taylor,	Catalysis in Theory and Practice,	948
Roth, Walter A., and Karl Scheel,	Konstanten der Atomphysik,	478
Schotz, S. P.,	Synthetic Rubber,	799
Schulze, A.,	Metallographie,	1439
Smith, Edgar F.,	Old Chemistries,	1599
Sommerfeld, Arnold,	Three Lectures on Atomic Physics,	1277
Stoner, E. C.,	Magnetism and Atomic Structure,	314
Sumner, James B.,	Textbook of Biological Chemistry,	788
Swarts, Fréd,	Cours de Chimie inorganique	1887
Taylor, H. S.,	Elementary Physical Chemistry,	1584
Teed, Frank L.,	Volume Alterations on and in Solution,	1760
Turner, D. M.,	Makers of Science. Electricity and Magnetism,	1598
Twenhofel, W. H.,	Treatise on Sedimentation,	1112
Washburn, E. W., Editor,	International Critical Tables, Vol. I,	144
von Weimarn, P. P.,	Die Allgemeinheit des Kolloidzustandes,	160
Weiser, Harry B.,	The Hydrous Oxides,	310
H. B. Weiser, Editor,	Colloid Symposium Monograph, Vol. IV,	467
Wood, J. K.,	The Chemistry of Dyeing,	1600

BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS
ORSAY

SUBJECT INDEX

Exclusive of New Books

Absolute zero of temperature, properties of substances and mixtures in the condensed state at the,..... 937
Absolute zero of temperature, properties at the, of the quantities associated with the reversible mixing of substances,..... 1559
Absolute zero of the externally controllable entropy, and internal energy of a substance or mixture,..... 747
Absorption of water by rubber, mechanism of the,..... 23
Acceptor-bromine-, silver sulphide hypothesis of latent image formation, thermodynamic possibilities of the,..... 1249
Acclimatization, positive and negative, phenomena of,..... 649
Acetic acid-stannic chloride solutions, specific volumes of, viscosities, electrical conductivities, and,..... 1420
Acetone and isopropyl alcohol, mixtures of, some physical chemical properties of,... 439
Acetone-iodine reaction in buffer solutions,..... 178
Acetylchloroaminobenzene, rate of transformation of, into o- and p-chloroanilides as a measure of the catalytic power of hydrochloric acid,..... 1192
Acetylene, hydrogenation of,..... 1332
Acid and salt, effect of, on rate of mutarotation,..... 882
Acid, arsenious, adsorption of, by precipitated ferric hydroxide,..... 419
Acid gel, silicic, function of water present in,..... 1230
Acid, hydrochloric, catalytic power of, rate of transformation of acetylchloroaminobenzene into o- and p- chloroanilides as a measure of the,..... 1192
Acids, adsorption of, alkali and salts by precipitated ferric hydroxide,..... 525
Acids and alkali, adsorptive powers of iron, aluminum and chromium hydroxides for, 1840
Acids, higher aliphatic, the effect of, on the surface tension of a heavy hydrocarbon oil,..... 543
Acids, naphthalene sulphonic, the optical identification of the, by means of their benzyl-pseudo-thiourea salts,..... 1082
Acids, compressibilities of aqueous solutions of, some fatty,..... 1521
Acid, acetic, and stannic chloride solutions, viscosities, electrical conductivities, and specific volumes of,..... 1420
Action of soaps, detergent, I, II,.....801, 1281
Activated molecules, on the nature of,..... 1433
Activation of halogen compounds, velocity of reaction and energy of,..... 535
Activities of aqueous solutions of sodium silicates, some vapor pressures and,..... 890
Activity, catalytic, of lead,..... 862
Activity, the catalytic, of metallized silica gels, I, II,.....1220, 1332
Activity, osmotic, lowering of vapor-pressures and freezing-points,..... 355
Adhesion and adhesives: gums, resins and waxes between polished metal surfaces,.. 1674
Adhesives and adhesion: gums, resins and waxes between polished metal surfaces,... 1674
Adsorbed vapor films, the thickness of,..... 897
Adsorbent, charcoal, ash-free, adsorption from solution by, III..... 1197
Adsorption and heat of adsorption of ammonia gas on metallic catalysts,..... 277
Adsorption by metallic hydroxides,.....419, 525, 686, 922
Adsorption by metallic hydroxides, a comparative study of the adsorptive powers of iron, aluminum, and chromium hydroxides for acids and alkali,..... 1840
Adsorption from solution by ash-free adsorbent charcoal, III,..... 1197
Adsorption by precipitated chromium hydroxides,..... 922
Adsorption equations,..... 251

Adsorption formula, discussion of the Freundlich,..... 1501
Adsorption by precipitated aluminum hydroxide,..... 686
Adsorption, Gibbs on,..... 1501
Adsorption, heat of, adsorption and, of ammonia gas on metallic catalysts,..... 277
Adsorption of acids, alkali and salts by precipitated ferric hydroxide,..... 525
Adsorption of arsenious acid by precipitated ferric hydroxide,..... 419
Adsorption of a solid-vapor interface, free energy change in,..... 719
Adsorption of carbon dioxide by charcoal, adsorption of gases by solids with special reference to the,..... 1601
Adsorption of electrolytes by manganese dioxide, and a discussion of the Freundlich adsorption formula,..... 997
Adsorption of gases by metallized silica gels,..... 88
Adsorption of gases by solids with special reference to the adsorption of carbon dioxide by charcoal,..... 1601
Adsorption of normal aliphatic alcohols from aqueous solution, the area of the internal surface of charcoal as determined by the,..... 641
Adsorption of typical dyes by basic mordants,..... 1704
Adsorption, studies in,..... 187, 649, 997
Adsorptive force of silica for water,..... 531
Adsorptive powers of iron, aluminum, and chromium hydroxides for acids and alkali, 1840
Air, bubbling, the ionization obtained by, through various solutions,..... 693
Alcohol, isopropyl, some physical chemical properties of mixtures of acetone and, ... 439
Alcohol, methyl, and mixtures of methyl alcohol and water, glucose equilibria in,..... 1880
Alcohol, methyl, and water, velocity of mutarotation of α glucose in,..... 742
Alcohol, methyl, heats of ionization in,..... 850
Alcohols, normal aliphatic, adsorption of, from aqueous solution, the area of the internal surface of charcoal as determined by the,..... 641
Aliphatic acids, higher, the effect of, on the surface tension of a heavy hydrocarbon oil,..... 543
Aliphatic alcohols, normal, adsorption of, from aqueous solution, the area of the internal surface of charcoal as determined by the,..... 641
Alizarin lakes,..... 1824
Alkali, acids and salts, adsorption of, by precipitated ferric hydroxide,..... 525
Alkali and acids, adsorptive powers of iron, aluminum and chromium hydroxides for, 1840
Alkali, aqueous, the hydrogen electrode in the study of the rate of saponification of oils and fats by,..... 131
Alkali halides, solutions of the, the partial molal volumes of water and salt in,..... 393
Alkali, salts and acids, adsorption of, by precipitated ferric hydroxide,..... 525
All-glass gas-circulating apparatus,..... 1099
Alumina-lime-silica system, studies on the,..... 607
Aluminum hydroxide, adsorption by precipitated, ... 686
Aluminum, iron and chromium hydroxides, adsorptive powers of, for acids and alkali,..... 1840
Aluminum-nickel-manganese-copper-alloys, a study of annealing effect of certain,... 1693
Ammonia gas, adsorption and heat of adsorption of, on metallic catalysts,..... 277
Ammonia, photosynthesis with,..... 1338
Ammonium hydroxide, carbonate and bicarbonate, solubility of copper sulphate, malachite, and burgundy precipitate in,..... 728
Amorphous materials, a study of the structural changes in,..... 1511
Aniline, the electrical conductivities of some solutions in,..... 547
Annealing effects of certain copper-nickel-aluminum-manganese alloys,..... 1693
Apparatus, an all-glass gas-circulating,..... 1099
Apparatus for the determination of melting temperature, a convenient form of,.... 1381
Apparent viscosity of colloidal solutions,..... 383
Application of the electron tube to potentiometric titrations,..... 519

Aqueous alkali, the hydrogen electrode in the study of the rate of saponification of oils and fats by,..... 131
Aqueous salts solutions, light-scattering of,..... 1150
Aqueous sodium silicate solutions, diffusion of, across semipermeable membranes,... 407
Aqueous solutions of sodium silicates,.....355, 511, 616
Aqueous solutions of sodium silicates, some vapor pressures and, activities of,..... 890
Aqueous solutions of some fatty acids, compressibilities of,..... 1521
Aqueous solutions containing organic indicators or inorganic salts, spectral transmission curves for some,..... 161
Aqueous solution, the area of the internal surface of charcoal as determined by the adsorption of normal aliphatic alcohols from,..... 641
Aqueous solutions, the effect of gelatin upon the size and distribution of macroscopic crystals grown from,..... 877
Arc, high-tension, nitrogen fixation by the,..... 1539
Area of the internal surface of charcoal as determined by the adsorption of normal aliphatic alcohols from aqueous solution, the,..... 641
Arsenious acid, adsorption of, by precipitated ferric hydroxide,..... 419
Ash-free adsorbent charcoal, adsorption from solution by,..... 1197
Ash-free and impure charcoal, a comparison of results obtained with,..... 1197
Atmospheric and pure nitrogen in distilled and sea water, on the solubility of,..... 81
Barium, beryllium, magnesium, calcium, and strontium, the electrode potentials of, from thermal data,..... 1267
Barium sulphate, the coalescence of an unfilterable precipitate of,..... 601
Basic viscosity of ice-cream mixes,..... 596
Basic viscosity of ice-cream mixes, effect of temperature on the,..... 1663
Basic mordants, adsorption of typical dyes by,..... 1704
Behavior, colloidal, of gelatine sols and gels, light-scattering capacity and,..... 764
Benzene-ethylbenzene and toluene-benzene mixtures, partial vapor pressures of,..... 1884
Benzene-toluene and benzene-ethylbenzene mixtures, partial vapor pressures of,..... 1884
Benzoate, methyl, a study of the ternary system, methanol, water and,..... 1050
Benzyl-pseudo-thiourea salts, the optical identification of the naphthalene sulphonic acids by means of their,..... 1082
Beryllium, magnesium, calcium, strontium and barium, the electrode potentials of, from thermal data,..... 1267
Bicarbonate, carbonate and ammonium hydroxide, solubility of copper sulphate, malachite, and burgundy precipitate in,..... 728
Biological transportation systems containing sulphur, influence of heat and hydrogen ion concentration on,..... 867
Bisulphide, carbon, and gasoline, some experimental results, particularly with,..... 1761
Bromide ion, mercurous bromide, and mercury electrode, electromotive force of the, an improved hydrogen electrode vessel and the,..... 886
Bromide, mercurous bromide ion and mercury electrode, an improved hydrogene lectrode vessel and the electromotive force of the,..... 886
Bromides, different, the comparison of emulsions made with,..... 906
Bromine-acceptor, silver sulphide hypothesis of latent image formation, thermodynamic possibilities of the,..... 1249
Bubbling air through various solutions, ionization obtained by,..... 693
Buffer solution, iodine-acetone reaction in,..... 178
Building materials, composition of, on the nature of the influence of humidity changes upon the,..... 564
Burgundy precipitate, copper sulphate, and malachite, solubility of, in ammonium hydroxide, carbonate and bicarbonate,..... 728
Calcium, beryllium, magnesium, strontium and barium, electrode potentials of, from thermal data,..... 1267
Capacity, light-scattering, and colloidal behavior of gelatine sols and gels,..... 764

Carbonate, ammonium, bicarbonate and hydroxide, solubility of copper sulphate, malachite and burgundy precipitate in,..... 728
Carbon bisulphide and gasoline, some experimental results particularly with,..... 1761
Carbon dioxide, adsorption of, by charcoal, adsorption of gases by solids with special reference to the,..... 1601
Carbon monoxide, refractivity of,..... 723
Catalysis, contact, fifth report of the committee on,..... 1121
Catalysis, metallic, adsorption and heat of adsorption of ammonia gas on,..... 277
Catalytic activity of lead,..... 862
Catalytic activity of metallized silica gels,..... 1220, 1332
Catalytic decomposition of esters by nickel, a study of the mechanism of,..... 102
Catalytic minimum point,..... 178
Catalytic power of hydrochloric acid, the rate of transformation of acetylchloroaminobenzene into o- and p-chloroanilides as a measure of the,..... 1192
Catalytic reactions of ethylene,..... 961
Causes of solubility, on the,..... 1742
Cell, electromotive force of the, with transference, and theory of interdiffusion of electrolytes,..... 1478
Cell mitosis,..... 430
Cells, photovoltaic, a study of,..... 1357
Cement, Portland, studies on the hydrolysis of compounds which may occur in, ... 1627
Cements, some remarks on the colloidal theory of,..... 933
Change, free energy, in adsorption at a solid-vapor interface,..... 719
Changes, humidity, on the nature of the influence of, upon the composition of building materials,..... 564
Changes, structural, in amorphous materials, a study of the,..... 1511
Charcoal, adsorption of gases by solids with special reference to adsorption of carbon dioxide by,..... 1601
Charcoal, ash-free adsorbent, adsorption from solution by,..... 1197
Charcoal, impure and ash-free, a comparison of results obtained with,..... 1197
Charcoal, the area of the internal surface of, as determined by the adsorption of normal aliphatic alcohols from aqueous solution,..... 641
Chemical potential, the mass unit of the,..... 69
Chemical, and some physical properties of mixtures of acetone and isopropyl alcohol, 439
Chemical reactivity, the signification of isocatalytic data and the so-called protion theory of,..... 1400
Chemistry, the physical, of color lake formation,..... 1383, 1704, 1824
Chloride, methylene, the vapor pressures of,..... 1737
Chloride, stannic, and acetic acid solutions, viscosities, electrical conductivities, and specific volumes of,..... 1420
Chlorides, nitrosyl, the thermal decomposition of,..... 374
o- and p-chloroanilides, the rate of transformation of acetylchloroaminobenzene into, as a measure of the catalytic power of hydrochloric acid,..... 1192
Chromate, silver, the color of,..... 931
Chromium, aluminum and iron hydroxides, adsorptive powers of, for acids and alkali, 1840
Chromium hydroxide, precipitated, adsorption by,..... 922
Chromium, iron and aluminum hydroxides, the adsorptive powers of, for acids and alkali,..... 1840
Circulating, gas-, an all-glass, apparatus,..... 1099
Coagulation, by electrolytes, influence of concentration of a sol on its,..... 187
Coagulation of sols by a mixture of electrolytes and the phenomena of positive and negative acclimatization,..... 649
Coalescence of an unfilterable precipitate of barium sulphate,..... 601

Colloidal behavior of gelatine sols and gels, the light-scattering capacity (Tyndall effect) and, ... 764
Colloidal iodine, ... 1091
Colloidal particles, sedimentation of, ... 1034
Colloidal solutions, apparent viscosity of, ... 383
Colloidal theory of cements, some remarks on the, ... 933
Colloids, on the relation of phenol to proteins and other, ... 1
Colorimetric estimation: diffusion, electrometric titrations, ... 616
Colorimetric standards, solutions for, ... 161
Color lake formation, the physical chemistry of, ... 1383, 1704, 1824
Color of silver chromate, the, ... 931
Colors, structural, in insects, ... 321, 1856
Combustion, heats of, investigation on the, of proposed secondary standard substances and on position and optical isomers, ... 58
Comparative study of the adsorptive powers of iron, aluminum and chromium hydroxides for acids and alkali, ... 1840
Comparing the times of mixing of two transparent liquids in different proportions, a method of, and some experimental results, ... 1761
Comparison of emulsions made with different bromides, ... 906
Comparison of results obtained with ash-free and impure charcoal, ... 1197
Committee on contact catalysis, fifth report of the, ... 1121
Composite yellow ... 1746
Composition of building materials, on the nature of the influence of humidity changes upon the ... 564
Compounds, halogen, the velocity of reaction and energy of activation of, ... 535
Compounds, hydrolysis of, which may occur in Portland cement, studies on the, ... 1627
Compounds, organic, some simple, the transition between the glassy and liquid states in the case of, ... 1842
Compounds, the positions of the K-absorption limits of vanadium in various of its, ... 703
Compressibilities of aqueous solutions of some fatty acids, ... 1521
Concentration, hydrogen ion, and influence of heat on biological transportation systems containing sulphur ... 867
Concentration of a sol on its coagulation by electrolytes, influence of, ... 187
Condensed state at the absolute zero of temperature, properties of substances and mixtures in the, ... 937
Conductivities, electrical, viscosities, and specific volumes of acetic acid-stannic chloride solutions, ... 1426
Conductivities, electrical, of some solutions in aniline, ... 547
Conductivity data, the correction of, for the conductivity of the solvent, ... 1647
Conductivity of the solvent, the correction of conductivity data for the, ... 1647
Contact catalysis, fifth report of the committee on, ... 1121
Contraction of molecules in the liquid state, on the, ... 1581
Controllable entropy, externally, the absolute zero of the, and internal energy of a substance or mixture, ... 747
Convenient form of apparatus for the determination of melting temperature, a, ... 1381
Copper number for glucose, ... 1441
Copper sulphate, malachite, and burgundy precipitate, solubility of, in ammonium hydroxide, carbonate, and bicarbonate, ... 728
Correction of conductivity data for the conductivity of the solvent, the, ... 1647
Corresponding states for the entropy of elements, ... 681
Creeping of solutions, ... 1246
Crystals, macroscopic, grown from aqueous solutions, the effect of gelatin upon the size and distribution of, ... 877
Curves, spectral transmission, for some aqueous solutions containing organic indicators or inorganic salts, ... 161

Data, conductivity, the correction of, for the conductivity of the solvent,..... 1647
Data, isocatalytic, the signification of, and the so-called protion theory of chemical reactivity,..... 1400
Data, thermal, the electrode potentials of beryllium, magnesium, calcium, strontium, and barium from,..... 1267
Decay of phosphorescence of zinc sulphide,..... 115
Decomposition, catalytic, of esters by nickel, a study of the mechanism of the,..... 102
Decomposition of hydrogen sulphide,..... 1212
Decomposition, photochemical, of hydrogen peroxide solutions,..... 1507
Decomposition, photochemical, of zinc sulphide, the rôle of water in the,..... 1237
Decomposition, thermal, of hydrogen peroxide,..... 1352
Decomposition, thermal, of nitrosyl chlorides,..... 374
Decomposition, thermal, of nitrogen pentoxide,..... 1572
Densities and solubilities of saturated solutions of sodium and potassium halides at 25°,..... 459
Detergent action of soaps,..... 801, 1281
Determination of melting temperatures, a convenient form of apparatus for the,..... 1381
Diabetes, relation between the metabolism of glucose and fats in,..... 1259
2, 6-Dibromobenzenoneindophenol,..... 1053
Dichromate, silver, in solid gelatin gel, the zone pattern formed by,..... 713
Diffusion: colorimetric estimation: electrometric titrations,..... 616
Diffusion of aqueous sodium silicate solutions across semipermeable membranes,..... 407
Dihalides of germanium,..... 1526
Dihalides of germanium, tin, and lead,..... 1817
Dioxide, carbon, adsorption of gases by solids with special reference to,..... 1601
Dioxide, germanium, preparation of, fused germanium directly from,..... 1429
Dioxide, manganese, adsorption of electrolytes by,..... 997
Dioxide, sulphur, and hydrogen sulphide, gaseous reaction between,..... 216
Discussion of the Freundlich adsorption formula,..... 997
Distilled and sea water, solubility of pure and atmospheric nitrogen in,..... 81
Distribution and size of macroscopic crystals grown from aqueous solutions, the effect of gelatin upon the,..... 877
Drop number and emulsifiability, the,..... 1263
Dyes, typical, adsorption of, by basic mordants,..... 1704
Dynamic method, an improved, for measuring vapor pressures,..... 231
Dynamic surface tension and the structure of surfaces,..... 207
Effect of acid and salt on rate of mutarotation,..... 882
Effect of gelatin upon the size and distribution of macroscopic crystals grown from aqueous solutions,..... 877
Effect of higher aliphatic acids on the surface tension of a heavy hydrocarbon oil,..... 543
Effect of monomolecular films on the evaporation of ether solutions,..... 1719
Effect, neutral salt,..... 291
Effect of temperature on the basic viscosity of ice-cream mixes,..... 1663
Effects, annealing of certain copper-nickel-aluminum-manganese alloys, a study of,.. 1693
Effect, Tyndall, and colloidal behavior of gelatin sols and gels,..... 764
Electrode, hydrogen, in the study of the rate of saponification of oils and fats by aqueous alkali,..... 131
Electrode potentials of beryllium, magnesium, calcium, strontium, and barium from thermal data, the..... 1267
Electrode vessel, hydrogen, an improved, and the electromotive force of the mercury, mercurous bromide, bromide ion electrode,..... 886
Electrolytes, adsorption of, by manganese dioxide, and a discussion of the Freundlich adsorption formula,..... 997
Electrolytes, influence of concentration of a sol on its coagulation by,..... 187
Electrolytes, coagulation of sols by a mixture of,..... 649

Electrolytes, electromotive force of the cell with transference and theory of interdiffusion of,... 1478
Electrometric titrations: diffusion: colorimetric estimation,... 616
Electromotive force of the cell with transference and theory of interdiffusion of electrolytes,... 1478
Electromotive force of the mercury, mercurous bromide, bromide ion electrode, an improved hydrogen electrode vessel and the,... 886
Electron tube, the application of the, to potentiometric titrations,... 519
Elements, entropy of, corresponding states for the,... 681
Emulsifiability, the drop number and,... 1263
Emulsification, Gibbs on,... 1681
Emulsification of solid powders,... 1566
Emulsions made with different bromides, the comparison of,... 906
Emulsion, the photographic,... 906
Energy change, free, in adsorption at a solid-vapor interface,... 719
Energy, free, of the elements, the internal energy, maximum work, and... 1669
Energy, the internal, maximum work, and free energy of the elements,... 1669
Energy, the internal, and the externally controllable entropy of a substance or mixture, the absolute zero of,... 747
Electrical conductivities, viscosities, and specific volumes of acetic acid-stannic chloride solutions,... 1420
Electrical conductivities of some solutions in aniline,... 547
Electrochemical studies of titanium, some,... 1404
Electrode, bromide ion, mercurous bromide and mercury, electromotive force of the 886
Elements, free energy of the, the internal energy, maximum work, and... 1669
Emulsion, the photographic,... 906
Energy and reation of activation of halogen compounds, the velocity of,... 535
Entropy, externally controllable, and internal energy of a substance or mixture, the absolute zero of the,... 747
Entropy of elements, corresponding states for the,... 681
Equations, adsorption,... 251
Equation, the Thomson,... 1798
Equilibria system, heterogeneous: Na_2O: SiO_2: H_2O, at 25°C,... 511
Equilibrium, the methane,... 124, 246, 417
Esters, catalytic decomposition of, by nickel, a study of the mechanism of the,... 102
Estimation, colorimetric: diffusion: electrometric titrations,... 616
Ether solutions, the effect of monomolecular films on the evaporation of,... 1719
Ethylbenzene-benzene and toluene-benzene mixtures, partial vapor pressures of,... 1884
Ethylene, catalytic reactions of,... 961
Ethylene, the hydrogenation of,... 1220
Evaporation of ether solutions, the effect of monomolecular films on the,... 1719
Examination, a critical, of certain filters for the 365 mercury line,... 1732
Experimental results, some, particularly with gasoline and carbon bisulphide,... 1761
Experimental technique of photochemistry, studies in the,... 1732
Externally controllable entropy and internal energy of a substance or mixture, the absolute zero of the,... 747
Fats and oils, the hydrogen electrode in the study of the rate of saponification of, by aqueous alkali,... 131
Fatty acids, compressibilities of aqueous solutions of some,... 1521
Fats and glucose in diabetes, relation between the metabolism of,... 1259
Ferric hydroxide, precipitated, adsorption of acids, alkali and salts by,... 525
Ferric hydroxide, precipitated, adsorption of arsenious acid by,... 419
Fifth report of the committee on contact catalysis,... 1121
Films, monomolecular, the effect of, on the evaporation of ether solutions,... 1719
Films, adsorbed vapor, the thickness of,... 897

Filters, certain, a critical examination of, for the 365 mercury line,..... 1732
Fixation, nitrogen, by the high-tension arc..... 1539
Force, the adsorptive, of silica for water,..... 531
Force, electromotive, of the cell with transference and theory of interdiffusion of electrolytes..... 1478
Force, electromotive, of the mercury, mercurous bromide, bromide ion electrode, an improved hydrogen electrode vessel and the,..... 886
Form of apparatus for the determination of melting temperature, a convenient,..... 1381
Formation, indophenol, a study of the velocity of,..... 1053
Formation, the physical chemistry of color lake, ... 1383, 1704, 1824
Formation, latent image, thermodynamic possibilities of the silver sulphide bromine-acceptor hypothesis of,..... 1249
Formation of Liesegang rings, studies in the,..... 481
Formula, adsorption, Freundlich, a discussion of the,..... 997
Free energy change in adsorption at a solid-vapor interface, the,..... 719
Free energy of the elements, the internal energy, maximum work, and,..... 1669
Freezing-points and vapor pressures, lowering of,..... 355
Freundlich adsorption formula, discussion of the,..... 997
Function of water present in silicic acid gel,..... 1230
Fused germanium, preparation of, directly from germanium dioxide,..... 1429
Gage for the measurement of high vacua,..... 591
Gas-circulating apparatus, an all-glass,..... 1099
Gaseous reaction between hydrogen sulphide and sulphur dioxide, the,..... 216
Gases, the adsorption of, by metallized silica gels,..... 88
Gases, the adsorption of, by solids with special reference to the adsorption of carbon dioxide by charcoal,..... 1601
Gasoline and carbon bisulphide, some experimental results, particularly with,..... 1761
Gel and as a sol, the imbibition of gelatin dried as a,..... 464
Gelatin gel, solid, the zone pattern formed by silver dichomate in,..... 713
Gelatin, the imbibition of, dried as a gel and as a sol,..... 464
Gelatin, optical rotation of, the influence of salts on the,..... 1873
Gelatin sols and gels, colloidal behavior of, light-scattering capacity and,..... 764
Gelatin-tannin reaction, the study of the,..... 448
Gelatin, the effect of, upon the size and distribution of macroscopic crystals grown from aqueous solutions..... 877
Gel, silica: a study of the structural changes in amorphous materials,..... 1511
Gel, silicic acid, the function of water present in,..... 1230
Gels, metallized silica, the adsorption of gases by,..... 88
Gels, metallized silica, the catalytic activity of,..... 1220, 1332
Germanium,..... 1101, 1429, 1526, 1716, 1817
Germanium dioxide, preparation of fused germanium directly from,..... 1429
Germanium, fused, preparation of, directly from germanium dioxide,..... 1429
Germanium monosulphide,..... 1716
Germanium tetrabromide, the vapor pressure of,..... 1101
Germanium, the dihalides of,..... 1526
Germanium, tin and lead, the dihalides of,..... 1817
Gibbs on adsorption,..... 1501
Gibbs on emulsification,..... 1681
Glass, all-, gas-circulating apparatus,..... 1099
Glass, studies on,..... 1842
Glassy and liquid states in the case of some simple organic compounds, the transition between the,..... 1842
Glucose, α, mutarotation of velocity of, in methyl alcohol and water,..... 742
Glucose, α and β, the relative velocities of mutarotation of,..... 882
Glucose and fats in diabetes, relation between the metabolism of,..... 1259

Glucose, the copper number for, ... 1441
Gums, resins, and waxes between polished metal surfaces, ... 1674
Halides, alkali, the partial molal volumes of water and salt in solutions of the, ... 393
Halides, potassium and sodium, the solubilities and densities of saturated solutions of, ... 448
Halogen compounds, the velocity of reaction and energy of activation of, ... 535
Heat and hydrogen concentration, influence of, on biological transportation systems containing sulphur, ... 867
Heat of adsorption and adsorption of ammonia gas on metallic catalysts, ... 277
Heats of combustion of proposed secondary standard substances, investigation on, and on position and optical isomers, ... 58
Heats of ionization in methyl alcohol, ... 850
Heavy hydrocarbon oil, the effect of higher aliphatic acids on the surface of a, ... 543
Heterogeneous equilibria system: Na_2O: SiO_2: H_2O, at 25°C, ... 511
Higher aliphatic acids, the effect of, on the surface tension of a heavy hydrocarbon oil, ... 543
High-tension arc, nitrogen fixation by the, ... 1539
High vacua, a gage for the measurement of, ... 591
Hydrocarbon oil, a heavy, the effect of higher aliphatic acids on the surface tension of, 543
Hydrochloric acid, catalytic power of, the rate of transformation of acetylchloroaminobenzene into o- and p- chloroanilides as a measure of the, ... 1192
Hydrogenation of acetylene, ... 1332
Hydrogenation of ethylene, ... 1220
Hydrogen electrode in the study of the rate of saponification of oils and fats by aqueous alkali, ... 131
Hydrogen electrode vessel, an improved, and the electromotive force of the mercury, mercurous bromide, bromide ion electrode, ... 886
Hydrogen ion concentration and heat, influence of, on biological transportation systems containing sulphur, ... 867
Hydrogen peroxide solutions, photochemical decomposition of, ... 1507
Hydrogen peroxide, thermal decomposition of, ... 1352
Hydrogen sulphide and sulphur dioxide, the gaseous reaction between, ... 216
Hydrogen sulphide, the decomposition of, ... 1212
Hydrolysis of compounds which may occur in Portland cement, studies on, ... 1627
Hydroxide, adsorption by precipitated aluminum, ... 686
Hydroxide, adsorption by precipitated chromium, ... 922
Hydroxide, adsorption of arsenious acid by precipitated ferric, ... 419
Hydroxide, adsorption of acids, alkali and salts by precipitated ferric, ... 525
Hydroxide, ammonium, carbonate and bicarbonate, solubility of copper sulphate, malachite, and burgundy precipitates in, ... 728
Hydroxides, iron, aluminum and chromium, adsorptive powers of, for acids and alkali, a comparative study of the, ... 1840
Hydroxides, metallic adsorption by, ... 419, 525, 686, 922, 1840
Hypothesis, silver sulphide bromine-acceptor, of latent image formation, thermodynamic possibilities of the, ... 1249
Humidity changes, on the nature of the influence of, upon the composition of building materials, ... 564
Ice-cream mixes, the basic viscosity of, ... 596
Ice-cream mixes, the effect of temperature on the basic viscosity of, ... 1663
Identification, optical, of the naphthalene sulphonic acids by mens of their benzyl-pseudo-thiourea salts, the, ... 1082
Image formation, latent, thermodynamic possibilities of the silver sulphide bromine-acceptor hypothesis of, ... 1249
Imbibition of gelatin dried as a gel and as a sol, ... 464
Improved dynamic method for measuring vapor pressure, ... 231

Improved hydrogen electrode vessel and the electromotive force of the mercury, mercurous bromide, bromide ion electrode,..... 886
Impure and ash-free charcoal, a comparison of results obtained with,..... 1197
Indicators, organic, or inorganic salts, spectral transmission curves for some aqueous solutions containing,..... 161
Indophenol formation, a study of the velocity of the,..... 1053
Influence of concentration of a sol on its coagulation by electrolytes,..... 187
Influence of heat and hydrogen ion concentration on biological transportation systems containing sulphur,..... 867
Influence of humidity changes upon the composition of building materials on the nature of the,..... 564
Influence of salts on the optical rotation of gelatin,..... 1873
Inorganic salts or organic indicators, spectral transmission curves for some aqueous solutions containing,..... 161
Insects, structural colors in,.....321, 1856
Integuments, iridescent,..... 1856
Interaction of ions, the velocity of,..... 1790
Interdiffusion of electrolytes, theory of,..... 1478
Interface, solid-vapor, the free energy change in adsorption at a,..... 719
Internal energy and externally controllable entropy of a substance or mixture, with absolute zero of the,..... 747
Internal energy, maximum work, and free energy of the elements,..... 1669
Internal surface of charcoal, the area of the, as determined by the adsorption of normal aliphatic alcohols from aqueous solution,..... 641
Investigation on the heats of combustion of proposed secondary standard substances and on position and optical isomers,..... 58
Iodine-acetone reaction in buffer solutions, the,..... 178
Iodine, colloidal,..... 1091
Ion concentration, hydrogen, influence of heat and, on biological transportation systems containing sulphur,..... 867
Ion, bromide, mercurous bromide and mercury electrode, the electromotive force of the, an improved hydrogen electrode vessel and the,.....850, 886
Ionization, heats of, in methyl alcohol,..... 850
Ionization obtained by bubbling air through various solutions,..... 693
Ionization produced by radon in spherical vessel,..... 1322
Ions, interaction of, the velocity of,..... 1790
Ions, silicate,..... 616
Iridescent integuments,..... 1856
Iron, aluminum and chromium hydroxides, adsorptive powers of, for acids and alkali,..... 1840
Iron in nature, studies on the transformation of,..... 626
Isocatalytic data and the so-called protion theory of chemical reactivity, the signification of,..... 1400
Isomers, optical, investigation on the heats of combustion of proposed secondary standard substances and on position and,..... 58
Isopropyl alcohol, mixtures of acetone and, some physical chemical properties of,... 439
K-absorption limits of vanadium in various of its compounds, the position of the,... 703
Laboratory study of nitrogen fixation by the high-tension arc, a,..... 1539
Lake, color, formation, the physical chemistry of,.....1383, 1704, 1824
Lakes, alizarin,..... 1824
Latent image formation, thermodynamic possibilities of the silver sulphide bromine-acceptor hypothesis of,..... 1249
Lead, catalytic activity of,..... 862
Lead, germanium, and tin, the dihalides of,..... 1817
Liesegang rings, studies in the formation of,..... 481

Light-scattering capacity (Tyndall effect) and colloidal behavior of gelatin sols and gels,..... 764
Light-scattering of aqueous salt solutions,..... 1150
Lime-alumina-silica, studies on the system,..... 607
Limits, K-adsorption, of vanadium in various of its compounds, the positions of the.. 703
Line, mercury, the 365, a critical examination of certain filters for,..... 1732
Liquid and glassy states in the case of some simple organic compounds, the transition between the,..... 1842
Liquid state, on the contraction of molecules in the,..... 1581
Liquids, two transparent, in different proportions, a method of comparing the times of mixing of,..... 1761
Lowering of vapor-pressures and freezing-points,..... 355
Macroscopic crystals grown from aqueous solutions, the effect of gelatine upon the size and distribution of,..... 877
Manganese dioxide, adsorption of electrolytes by,..... 997
Manganese-copper-nickel-aluminum alloys, a study of annealing effect of certain,... 1693
Magnesium, calcium, strontium, beryllium, and barium, the electrode potentials of, from thermal data,..... 1267
Malachite, copper sulphate and burgundy precipitate, solubility of, in ammonium hydroxide, carbonate and bicarbonate,..... 728
Mass unit of the chemical potential,..... 69
Materials, amorphous, a study of the structural changes in,..... 1511
Materials, building, on the nature of the influence of humidity changes upon the composition of,..... 564
Maximum work, internal energy and free energy of the elements,..... 1669
Measurement of high vacua, a gage for the,..... 591
Mechanism of the absorption of water by rubber,..... 23
Mechanism of the catalytic decomposition of esters by nickel, a study of the,..... 102
Melting temperature, a convenient form of apparatus for the determination of,..... 1381
Membranes, semipermeable, diffusion of aqueous sodium silicate solutions across,... 407
Mercurous bromide, bromide ion and mercury electrode, the electromotive force of the, an improved hydrogen electrode vessel and,..... 886
Mercury line, the 365, a critical examination of certain filters for,..... 1732
Mercury, mercurous bromide, bromide ion electrode, the electromotive force of the, an improved hydrogen electrode vessel and,..... 886
Metabolism of glucose and fats in diabetes, relation between the,..... 1259
Metallic catalysts, adsorption and heat of adsorption of ammonia gas on..... 277
Metallic hydroxides, adsorption by,..... 419, 525, 686, 922, 1840
Metallized silica gels, the adsorption of gases by,..... 88
Metallized silica gels, the catalytic activity of,..... 1220, 1332
Metal surfaces, polished, gums, resins and waxes, between,..... 1674
Methane equilibrium, the..... 124, 246, 417
Methanol, methyl benzoate and water, a study of the ternary system,..... 1050
Method, dynamic, an improved, for measuring vapor pressures,..... 231
Method for comparing the times of mixing of two transparent liquids in different proportions, and some experimental results, particularly with gasoline and carbon bisulphide,..... 1761
Methyl alcohol and water, velocity of mutarotation of α glucose in,..... 742
Methyl alcohol, heats of ionization in,..... 850
Methyl benzoate, methanol and water, a study of the ternary system,..... 1050
Methylene chloride, the vapor pressures of,..... 1737
Minimum point, the catalytic,..... 178
Mitosis, cell,..... 430
Mixes, ice-cream, the basic viscosity of,..... 596
Mixes, ice-cream, the effect of temperature on the basic viscosity of,..... 1663

Mixing of substances, reversible, properties at the absolute zero of temperature of the quantities associated with the,..... 1559
Mixing of two transparent liquids in different proportions, times of, a method of comparing the,..... 1761
Mixture of electrolytes, coagulation of sols by a, and the phenomena of positive and negative acclimatization,..... 649
Mixtures, benzene-toluene and benzene-ethylbenzene, partial vapor pressures of,... 1884
Mixtures and substances in the condensed state, properties of, at the absolute zero of temperature,..... 937
Mixtures of acetone and isopropyl alcohol, some physical chemical properties of,.... 439
Molal volumes of water, the partial, and salt in solutions of the alkali halides,..... 393
Molecules, activated, on the nature of,..... 1433
Molecules, on the contraction of, in the liquid state,..... 1581
Monomolecular films on the evaporation of ether solutions, the effect of,..... 1719
Monosulphide, germanium,..... 1716
Monoxide, carbon, the refractivity of,..... 723
Mordants, basic, adsorption of typical dyes by,..... 1704
Mutarotation,..... 742, 882, 1880
Mutarotation of α glucose in methyl alcohol and water, velocity of,..... 742
Mutarotation of α and β glucose, relative velocities of,..... 882
Naphthalene sulphonic acids, the optical identifical of the, by means of their benzol-pseudo-thiourea salts,..... 1082
Nature, iron in, studies on the formation of,..... 626
Nature of activated molecules, on the,..... 1433
Nature of the influence of humidity changes upon the composition of building materials, on the,..... 564
Negative and positive acclimatization, the phenomena of,..... 649
Neutral salt effect,..... 291
New thermoregulator,..... 1097
Nickel, catalytic decomposition of esters by, a study of the mechanism of the,..... 102
Nitrogen pentoxide, thermal decomposition of, a study of the,..... 1572
Nitrosyl chlorides, the thermal decomposition of,..... 374
Nitrogen fixation by the high-tension arc,..... 1539
Nitrogen, pure and atmospheric, on the solubility of, in distilled and sea water,..... 81
Normal aliphatic alcohols, the adsorption of, from aqueous solutions, the area of the internal surface of charcoal as determined by the,..... 641
Number, copper, for glucose,..... 1441
Number, the drop, and emulsifiability,..... 1263
Observations on the system phenol-water, some,..... 1316
Oil, heavy hydrocarbon, the surface tension of a, the effect of higher aliphatic acids on,..... 543
Oils and fats, saponification of, by aqueous alkali, the hydrogen electrode in the study of the rate of,..... 131
Optical identification of the naphthalene sulphonic acids by means of their benzyl-pseudo-thiourea salts, the,..... 1082
Optical isomers and position, heats of combustion of proposed secondary standard substances and on, investigation on the,..... 58
Optical rotation of gelatin, influence of salts on the,..... 1873
Organic compounds, some simple, the transition between the glassy and liquid states in the case of,..... 1842
Organic indicators or inorganic salts, spectral transmission curves for some aqueous solutions containing,..... 161
Osmotic activity, lowering of vapor-pressures and freezing-points,..... 355
Partial molal volumes of water and salt in solutions of the alkali halides, the,..... 393
Partial vapor pressures of benzene-toluene and benzene-ethyl-benzene mixtures,.... 1884

Particles, colloidal, sedimentation of,..... 1034
Particle size, the relation of, to vapor pressure,..... 1798
Pattern, zone, formed by silver dichromate in solid gelatine gel,..... 713
Pentoxide, nitrogen, thermal decomposition of,..... 1572
Peroxide, hydrogen, solutions, the photochemical decomposition of,..... 1507
Peroxide, hydrogen, thermal decomposition of,..... 1352
Phenol, on the relation of, to proteins and other colloids,..... 1
Phenol tests,..... 1053
Phenol-water, some observations on the system,..... 1316
Phenol-water, the system,..... 757
Phenomena of positive and negative acclimatization, coagulation of sols by a mixture of electrolytes and the,..... 649
Phosphorescence of zinc sulphide, the decay of,..... 115
Photochemical decomposition of hydrogen peroxide solutions,..... 1507
Photochemical decomposition of zinc sulphide, the rôle of water in the,..... 1237
Photochemistry, experimental technique of, studies in the,..... 1732
Photographic emulsion, the,..... 906
Photosynthesis with ammonia,..... 1338
Photovoltaic cells, a study of,..... 1357
Physical-chemical properties of mixtures of acetone and isopropyl alcohol, some,..... 439
Physical chemistry of color lake formation,..... 1704, 1824
Point, the catalytic minimum,..... 178
Polished metal surfaces, gums, resins and waxes between,..... 1674
Portland cement, studies on the hydrolysis of compounds which may occur in,..... 1627
Position and optical isomers, investigation on the heats of combustion of proposed secondary standard substances and on,..... 58
Positions of the K-absorption limits of vanadium in various of its compounds, the..... 703
Positive and negative acclimatization, the phenomena of,..... 649
Possibilities, thermodynamic, of the silver sulphide bromine-acceptor hypothesis of latent image formation,..... 1249
Potassium and sodium halides at 25°, solutions of,..... 459
Potential, chemical, the mass unit of the,..... 69
Potentials, electrode, of beryllium, magnesium, calcium, strontium and barium from thermal data,..... 1267
Potentiometric titrations, the application of the electron tube to,..... 519
Powders, solid, emulsification of,..... 1566
Power, catalytic, of hydrochloric acid, the rate of transformation of acetylchloroaminobenzene into o- and p-chloroanilides as a measure of the,..... 1192
Powers, adsorptiive, of iron, aluminum and chromium hydroxides for acids and alkali, a comparative study of the,..... 1840
Precipitated aluminum hydroxide, adsorption by,..... 686
Precipitated chromium hydroxide, adsorption by,..... 922
Precipitated ferric hydroxide, adsorption of acids, alkali and salts by,..... 525
Precipitated ferric hydroxide, adsorption of arsenious acid by,..... 419
Precipitate, copper sulphate, malachite and burgundy, solubility of, in ammonium hydroxide, carbonate and bicarbonate,..... 728
Precipitate of barium sulphate, unfilterable, the coalescence of an,..... 601
Preparation of fused germanium directly from germanium dioxide,..... 1429
Pressures, partial vapor, of benzene-toluene and benzene-ethylbenzene mixtures,... 1884
Pressure, vapor, of germanium tetrabromide, the,..... 1101
Pressures, vapor, and freezing points, osmotic activity, lowering of,..... 354
Pressures, vapor, some, and activities of aqueous solutions of sodium silicates,..... 890
Pressure, vapor, the relation of particle size to,..... 1798
Pressures, vapor, of methylene chloride, the,..... 1737

Properties at the absolute zero of temperature of the quantities associated with the reversible mixing of substances, ... 1559
Properties of substances and mixtures in the condensed state at the absolute zero of temperature, ... 937
Properties, some physical chemical, of mixtures of acetone and isopropyl alcohol, ... 439
Proportions, different, two transparent liquids in, a method of comparing the times of mixing of, ... 1761
Proteins and other colloids, on the relation of phenol to, ... 1
Protion theory, so-called, of chemical reactivity, the signification of isocatalytic data and the, ... 1400
Pure and atmospheric nitrogen, on the solubility of, in distilled and sea water, ... 81
Quantities associated with the reversible mixing of substances, properties at the absolute zero of temperature of the, ... 1559
Radon in spherical vessels, ionization produced by, ... 1322
Rate of saponification of oils and fats by aqueous alkali, the hydrogen electrode in the study of the, ... 131
Rate of transformation of acetylchloroaminobenzene into o- and p-chloroanilides as a measure of the catalytic power of hydrochloric acid, the, ... 1192
Reactions of ethylene, catalytic, ... 961
Reaction, the velocity of, and energy of activation of halogen compounds, ... 535
Reaction, the gaseous, between hydrogen sulphide and sulphide dioxide, ... 216
Reaction, the iodine-acetone, in buffer solutions, ... 178
Reaction, tannin-gelatin, the study of the, ... 448
Reactivity, chemical, the so-called protion theory of, the signification of isocatalytic data and, ... 1400
Refractivity of carbon monoxide, ... 723
Relation between the metabolism of glucose and fats in diabetes, ... 1259
Relation of phenol to proteins and other colloids, on the, ... 1
Relation of vapor pressure to particle size, ... 1798
Relative velocities of mutarotation of α and β glucose; effect of acid and salt, ... 882
Remarks on the colloidal theory of cements, some, ... 933
Report, fifth, of the committee on contact catalysis, ... 1121
Resins, gums, and waxes between polished metal surfaces, ... 1674
Results, some experimental, on time of mixing, particularly with gasoline and carbon disulphide, ... 1761
Reversible mixing of substances, quantities associated with the, properties at the absolute zero of temperature of the, ... 1559
Rings, Liesegang, studies in the formation of, ... 481
Rôle of water in the photochemical decomposition of zinc sulphide, ... 1237
Rotation, optical, of gelatin, influence of salts on the, ... 1873
Rubber, the mechanism of the absorption of water by, ... 23
Salt and acid, effect of, on rate of mutarotation, ... 882
Salt and water in solutions of the alkali halides, the partial molal volumes of, ... 393
Salt effect, the neutral, ... 291
Salts, alkali and acids, adsorption of, by precipitated ferric hydroxide, ... 525
Salts, benzyl-pseudo-thiourea, the optical identification of the naphthalene sulphonic acids by means of their, ... 1082
Salts, the influence of, on the optical rotation of gelatin, ... 1873
Salts, inorganic, or organic indicators, spectral transmission curves for some aqueous solutions containing, ... 161
Salt solutions, aqueous, light-scattering of, ... 1150
Saponification of oils and fats by aqueous alkali, rate of, the hydrogen electrode in the study of the, ... 131
Saturated solutions of sodium and potassium halides at 25°, the solubilities and densities of, ... 459

Scattering capacity, light-, and colloidal behavior of gelatine sols and gels,..... 764
Scattering, light-, of aqueous salt solutions,..... 1150
Sea and distilled water, on the solubility of pure and atmospheric nitrogen in,..... 81
Secondary standard substances, proposed, investigation on the heats of combustion of, position and optical isomers,..... 58
Sedimentation of colloidal particles,..... 1034
Semipermeable membranes, diffusion of aqueous sodium silicate solutions across,..... 407
Signification of isocatalytic data and the so-called protion theory of chemical reactivity,..... 1400
Silica gel, a study of the structural changes in amorphous materials,..... 1511
Silica gels, metallized, the adsorption of gases by,..... 88
Silica gels, metallized, catalytic activity of,.....1220, 1332
Silica-lime-alumina, studies on the system,..... 607
Silica, the adsorptive force of, for water,..... 531
Silicate, aqueous sodium, solutions, diffusion of, across semipermeable membranes,.. 407
Silicate ions,..... 616
Silicates, sodium, aqueous solutions of,.....355, 511, 616
Silicates, sodium, aqueous solutions of, some vapor pressures and activities of,..... 890
Silicates, sodium, aqueous solutions of,..... 616
Silicic acid gel, the function of water present in,..... 1230
Silver chromate, the color of,..... 931
Silver dichromate in solid gelatin gel, the zone pattern formed by,..... 713
Silver sulphide bromine-acceptor hypothesis of latent image formation, thermodynamic possibilities of the,..... 1249
Size and distribution of macroscopic crystals grown from aqueous solutions, the effect of gelatin upon the,..... 877
Size, particle, the relation of, to vapor pressure,..... 1798
Soaps, detergent action of,.....801, 1281
Sodium and potassium halides at 25°, the solubilities and densities of saturated solutions of,..... 459
Sodium silicates, aqueous solutions of,.....355, 511, 616
Sodium silicate solutions, aqueous, diffusion of, across semipermeable membranes,.. 407
Sodium silicates, aqueous solutions of, some vapor pressures and activities of,..... 890
Sodium sulphate-water, the system,..... 496
Solid gelatine gel, the zone pattern formed by silver dichromate in,..... 713
Solid powers, emulsification of,..... 1566
Solids, the adsorption of gases by, with special reference to the adsorption of carbon dioxide by charcoal,..... 1601
Solid-vapor interface, the free energy change in adsorption at a,..... 719
Sol, the imbibition of gelatine dried as a gel and as a sol,..... 464
Sol, concentration of a, on its coagulation by electrolytes, influence of,..... 187
Sols, coagulation of, by a mixture of electrolytes and the phenomena of positive and negative acclimatization,..... 649
Sols and gels, gelatine, the light-scattering capacity (Tyndall effect) and colloidal behavior of,..... 764
Solubilities and densities of saturated solutions of sodium and potassium halides at 25°,..... 459
Solubility of copper sulphate, malachite and burgundy precipitate in ammonium hydroxide, carbonate and bicarbonate,..... 728
Solubility of pure and atmospheric nitrogen in distilled and sea water, on the,..... 81
Solubility, on the causes of,..... 1742
Solution, adsorption from, by ash-free adsorbent charcoal,..... 1197
Solution, aqueous, the area of the internal surface of charcoal as determined by the adsorption of normal aliphatic alcohols from,..... 641
Solutions, buffer, the iodine-acetone reaction in,..... 178

Solutions, acetic acid-stannic chloride, viscosities, electrical conductivities and specific volumes of, ... 1420
Solutions, aqueous, of sodium silicates, ... 355, 511, 616
Solutions, aqueous salt, light-scattering of, ... 1150
Solutions, aqueous sodium silicate, diffusion of, across semipermeable membranes, .. 407
Solutions, aqueous, spectral transmission curves for some, containing organic indicators, or inorganic salts, ... 161
Solutions, aqueous, the effect of gelatin upon the size and distribution of macroscopic crystals grown from, ... 877
Solutions, colloidal, the apparent viscosity of, ... 383
Solutions, ether, the effect of monomolecular films on the evaporation of, ... 1719
Solutions for colorimetric standards, ... 161
Solutions in aniline, the electrical conductivities of some, ... 547
Solutions of sodium and potassium halides at 25°, saturated, the solubilities and densities of, ... 459
Solutions of sodium silicates, aqueous, some vapor pressures and activities of, ... 890
Solutions, aqueous, of some fatty acids, compressibilities of, ... 1521
Solutions of the alkali halides, the partial molal volumes of water and salt in, ... 393
Solutions, hydrogen peroxide, the photochemical decomposition of, ... 1507
Solutions, the creeping of, ... 1246
Solutions, various, the ionization obtained by bubbling air through, ... 693
Solvent, conductivity of the, the correction of conductivity data for the, ... 1647
Specific volumes of acetic acid-stannic chloride solutions, viscosities, electrical conductivities and, ... 1420
Spectral transmission curves for some aqueous solutions containing organic indicators or inorganic salts, ... 161
Spherical vessels, ionization produced by radon in, ... 1322
Standards, colorimetric, solutions for, ... 161
Standard substances, proposed secondary, investigation on the heats of combustion of, and on position and optical isomers, ... 58
State, condensed, at the absolute zero of temperature, properties of substances and mixtures in the, ... 937
State, liquid, on the contraction of molecules in the, ... 1581
States, corresponding, for the entropy elements, ... 681
States, liquid and glassy, in the case of some simple organic compounds, the transition between the, ... 1842
Strontium, beryllium, magnesium, calcium, and barium, the electrode potentials of, from thermal data, ... 1267
Structural changes in amorphous materials, a study of the, ... 1511
Structural colors in insects, ... 321, 1856
Structure of surfaces, dynamic surface tension and the, ... 207
Studies in adsorption, ... 187, 649, 997
Studies in experimental technique of photochemistry, ... 1732
Studies in the formation of Liesegang rings, ... 481
Studies of titanium, some electrochemical, ... 1404
Studies on glass, ... 1842
Studies on the hydrolysis of compounds which may occur in Portland cement, ... 1627
Studies on the system lime-alumina-silica, ... 607
Studies on the transformation of iron in nature, ... 626
Study, a comparative, of the adsorptive powers of iron, aluminum, and chromium hydroxides for acids and alkali, ... 1840
Study of annealing effect of certain copper-nickel-aluminum-manganese alloys, ... 1693
Study of nitrogen fixation by the high-tension arc, a laboratory, ... 1539
Study of photovoltaic cells, ... 1357
Study of the mechanism of the catalytic decomposition of esters by nickel, ... 102

Study of the saponification of oils and fats by aqueous alkali, the hydrogen electrode in the, ... 131
Study of the structural changes in amorphous materials: silica gel, ... 1511
Study of the tannin-gelatin reaction, ... 448
Study of the ternary system: methyl benzoate, methanol, and water, ... 1050
Study of the thermal decomposition of nitrogen pentoxide, a, ... 1572
Study of the velocity of indophenol formation, ... 1053
Substance or mixture, externally controllable entropy and internal energy of a, the absolute zero of the, ... 747
Substances and mixtures in the condensed state at the absolute zero of temperature, properties of, ... 937
Substances, reversible mixing of, properties at the absolute zero of temperature of the quantities associated with the, ... 1559
Substances, secondary standard, proposed, investigation on the heats of combustion of, and on position and optical isomers, ... 58
Sulphate, barium, the coalescence of an unfilterable precipitate of, ... 601
Sulphate, copper, malachite and burgundy precipitate, solubility of, in ammonium hydroxide, carbonate and bicarbonate, ... 728
Sulphate, sodium, and water, ... 496
Sulphide, hydrogen, and sulphur dioxide, the gaseous reaction between, ... 216
Sulphide, hydrogen, decomposition of, ... 1212
Sulphide, silver, bromine-acceptor hypothesis of latent image formation, thermodynamic possibilities of the, ... 1249
Sulphide, zinc, the decay of phosphorescence of, ... 115
Sulphonic acids, naphthalene, the optical identification of the, by means of their benzyl-pseudo-thiourea salts, ... 1082
Sulphur, biological transportation systems containing influence of heat and hydrogen ion concentration on, ... 867
Sulphur dioxide and hydrogen sulphide, the gaseous reaction between, ... 216
Surface of charcoal, internal, the area of the, as determined by the adsorption of normal aliphatic alcohols from aqueous solution, ... 641
Surfaces, polished metal, gums, resins and waxes between, ... 1674
Surfaces, structure of, dynamic surface tension and the, ... 207
Surface tension, dynamic, and the structure of surfaces, ... 207
Surface tension of a heavy hydrocarbon oil, the effect of higher aliphatic acids on the, 543
System, heterogeneous equilibria, Na_2O, SiO_2, H_2O at 25°C, ... 511
System lime-alumina-silica, studies on the, ... 607
System ternary, a study of the: methyl benzoate, methanol, and water, ... 1050
System phenol-water, some observations on the, ... 1316
Systems, biological transportation, containing sulphur, influence of heat and hydrogen ion concentration on, ... 867
System sodium sulphate-water, ... 496
System water-phenol, ... 757
Tannin-gelatin reaction, the study of the, ... 448
Technique, experimental, of photochemistry, studies in the, ... 1732
Temperature, absolute zero of, properties at the, of the quantities associated with the reversible mixing of substances, ... 1559
Temperature, absolute zero of, properties of substances and mixitures in the condensed state at the, ... 937
Temperature, the effect of, on the basic viscosity of ice-cream mixes, ... 1663
Temperature, melting, a convenient form of apparatus for the determination of, ... 1381
Tension, surface, dynamic, and the structure of surfaces, ... 207
Tension, surface, of a heavy hydrocarbon oil, the effect of higher aliphatic acids on the 543
Ternary system, a study of the: methyl benzoate, methanol, and water, ... 1050
Tests, phenol, ... 1053

Tetrabromide, germanium, the vapor pressure of, ... 1101
Theoretical considerations, studies on the transformation of iron in nature, ... 626
Theory, colloidal, of cements, some remarks on the, ... 933
Theory of interdiffusion of electrolytes, electromotive force of the cell with transference, and, ... 1478
Theory, so-called protion, of chemical reactivity, the signification of isocatalytic data and the, ... 1400
Thermal data, the electrode potentials of beryllium, magnesium, calcium, strontium, and barium from, ... 1267
Thermal decomposition of hydrogen peroxide, ... 1352
Thermal decomposition of nitrogen pentoxide, a study of the, ... 1572
Thermal decomposition of nitrosyl chlorides, ... 374
Thermodynamic possibilities of the silver sulphide bromine-acceptor hypothesis of latent image formation, ... 1249
Thermoregulator, a new, ... 1097
Thickness of adsorbed vapor films, ... 897
Thomson equation, ... 1798
Times of mixing of two transparent liquids in different proportions, a method of, ... 1761
Tin, germanium, and lead, the dihalides of, ... 1817
Titanium, some electrochemical studies of, ... 1404
Titrations, electrometric: diffusion: colorimetric estimation, ... 616
Titrations, potentiometric, the application of the electron tube to, ... 519
Toluene-benzene and benzene-ethylbenzene mixtures, partial vapor pressures of, ... 1884
Transference and theory of interdiffusion of electrolytes, electromotive force of the cell with, ... 1478
Transformation of acetylchloroaminobenzene into o- and p-chloroanilides as a measure of the catalytic power of hydrochloric acid, the rate of, ... 1192
Transformation of iron in nature, studies on the, ... 626
Transition between the glassy and liquid states in the case of some simple organic compounds, the, ... 1842
Transmission curves, spectral, for some aqueous solutions containing organic indicators or inorganic salts, ... 161
Transparent liquids, two, in different proportions, a method of comparing the time of mixing, ... 1761
Transportation systems, biological, containing sulphur, influence of heat and hydrogen concentration on, ... 867
Two transparent liquids in different proportions, a method of comparing the times of mixing of, ... 1761
Tube, electron ,the application of the, to potentiometric titrations, ... 519
Tyndall effect and colloidal behavior of gelatine sols and gels, ... 764
Typical dyes, adsorption of, by basic mordants, ... 1704
Unfilterable precipitate of barium sulphate, the coalescence of an, ... 601
Unit, the mass, of the chemical potential, ... 69
Vacua, high, a gage for the measurement of, ... 591
Vanadium, the positions of the K-absorption limits, of, in various of its compounds, .. 703
Vapor films, the thickness of adsorbed, ... 897
Vapor, solid, interface, the free energy change in adsorption at a 719
Vapor pressure of germanium tetrabromide, ... 1101
Vapor pressures and activities of aqueous solutions of sodium silicates, some, ... 890
Vapor-pressures and freezing-points, lowering of, ... 355
Vapor pressures, an improved dynamic method for measuring, ... 231
Vapor pressures of methylene chloride, ... 1737
Vapor pressures, partial, of benzene-toluene and benzene-ethylbenzene mixtures, ... 1884
Vapor pressure, the relation of, to particle size, ... 1798
Velocities, relative, of mutarotation of α and β glucose, ... 882

Velocity of indophenol formation, a study of the, ... 1053
Velocity of interaction of ions, ... 1790
Velocity of mutarotation of α glucose in methyl alcohol and water, ... 742
Velocity of reaction and energy of activation of halogen compounds, the, ... 535
Vessel, hydrogen electrode, an improved, and the electromotive force of the mercury, mercurous bromide, bromide ion electrode, ... 886
Vessels, spherical, ionization produced by radon in, ... 1322
Viscosities, electrical conductivities, and specific volumes of acetic acid-stannic chloride solutions, ... 1420
Viscosity, the apparent, of colloidal solutions, ... 383
Viscosity, the basic, of ice-cream mixes, ... 596
Viscosity, the basic, of ice-cream mixes, the effect of temperature on, ... 1663
Volumes, specific, of acetic acid-stannic chloride solutions, viscosities, electrical conductivities, and, ... 1420
Volumes, partial molal, of water and salt in solutions of the alkali halides, the, ... 393
Water, absorption of, by rubber, the mechanism of the, ... 23
Water and methyl alcohol, velocity of mutarotation of α glucose in, ... 742
Water and salt in solutions of the alkali halides, the partial molal volumes of, ... 393
Water, adsorptive force of silica for, ... 531
Water, distilled and sea, pure and atmospheric nitrogen in, on the solubility of, ... 81
Water, methyl benzoate, methanol and, a study of the ternary system, ... 1050
Water-phenol, some observations on the system, ... 1316
Water-phenol, the system, ... 1316
Water present in silicic acid gel, the function of, ... 1230
Water, the rôle of, in the photochemical decomposition of zinc sulphide, ... 1237
Water-sodium, sulphate, the system, ... 496
Waxes, gums, and resins, between polished metal surfaces, ... 1674
Work, maximum, the internal energy, and free energy of the elements, ... 1669
Yellow, composite, ... 1746
Zero, absolute, of temperature, properties at the, of the quantities associated with the reversible mixing of substances, ... 1559
Zero, absolute, of temperature, properties of substances and mixtures in the condensed state at the, ... 937
Zero, the absolute, of the externally controllable entropy and internal energy of a substance or mixture, ... 747
Zinc sulphide, the decay of phosphorescence of, ... 115
Zinc sulphide, the rôle of water in the photochemical decomposition of, ... 1237
Zone pattern formed by silver dichromate in solid gelatine gel, ... 713

BIBLIOTHÈQUES DE L'UNIVERSITÉ DE PARIS
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